

Investigation of voltammetric procedures used in the ultra-trace determination and speciation of chromium III and VI.

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By

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Declaration

I declare that this Dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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18th day of January, 2005

ABSTRACT

Complexation of Cr^{III} was studied using the ligand 2, 2'-Bipyridyl (Bpy). Potentiometric titration was used in the modelling of Cr^{III} -Bpy complexes and establishment of complex stability constants by use of ESTA software package. Investigation of the mechanism involved in the voltammetric determination of chromium by adsorptive cathodic stripping voltammetry (AdCSV) showed different behavior of chromium in 0.1 M ammonium buffer when compared to a neutral electrolyte (0.1 M sodium nitrate). Alternating current voltammetry (ACV) showed evidence of Bpy adsorption on the electrode surface (HMDE) whereas Cr^{III} did not show any adsorption evidence but complexes of Cr^{III} -Bpy were also adsorbed onto the electrode. Cyclic voltammogram (CV) of Bpy exhibits a reversible process and Cr^{III} was characterized by a quasireversible process.

Cr^{III} -Bpy is investigated here as a model metal-ligand system used in analytical procedure. A set of generalized requirements for the determination of Cr^{III} by AdCSV is proposed and discussed. It is anticipated that the generalized requirements will be applicable to

any metal-ligand system used by that analytical technique. It is assumed that it should lead to an "educated" choice of a suitable ligand in order to increase selectivity and improve the detection limit in ultra trace analysis (ppb-ppt levels) by AdCSV.

Dedication

To my God,
my family,
and friends.

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List of Symbols

GTF : glucose tolerance factor

IR : insulin receptor

I : Insulin

LMWCr : Low-Molecular-Weight Chromium Binding-Substance

DNA : deoxyribonucleic acid

ehba : 2-ethyl-2-hydroxybutanoato

μg : microgram

mg : milligram

mV : millivolt

nM : nanomole

mol : mole

M : molar

L : liter

g : gram

pH : hydrogen potential

EMF : electro motive force

V : volt

ppt : part per trillion

Bpy : 2, 2' Bipyridyl

CDTA : Diaminocyclohexanetetraacetic acid

EDTA : Ethylenediaminetetraacetic acid

DTPA : Diethylenetriaminepentaacetic acid

DPCI : Diphenylcarbazide
 DPCO : Diphenylcarbazone
 DMCPE: Diphenylcarbazide-Modified Carbon Paste
 Electrode
 HMDE : Hanging Mercury Drop Electrode
 CV : Cyclic Voltammetry
 DP : Differential Pulse
 ACV : Alternating Current Voltammetry
 E_g : Potential of glass electrode
 T_i^r : calculated total concentration of component i
 T_i^c : real (analytical) concentration of component i
 r_{ij} : stoichiometric coefficient of coefficient of
 component i in complex j
 C_i^V : initial concentration of component i in
 titration vessel
 C_{im}^B : concentration of component i in solution burette
 m
 V_m : volume added from burette m
 V^0 : initial volume in vessel
 NC : number of components appearing in complexes
 E_k^0 : electrode response intercept
 E_k^{IS} : electrode selectivity
 E_k^{LJ} : liquid junction potential

- S_k : electrode response
 γ_k : activity coefficient of the electrode ion
 K_{ki} : selectivity coefficient of component i
 α : ionic size parameter
 Z_i : charge on species i
 λ_i^s : ionic conductance of species i in the test solution
 λ_i^b : ionic conductance of species i in the bridge solution
 $\{S_i^s\}$: activity of the species i in the test solution
 $\{S_i^b\}$: activity of the species i in the bridge solution
 $E_k^{LJ_0}$: the liquid junction between the bridge solution and a solution containing the bridge ions at the reference ionic strength
 H_T : total hydrogen ion concentration
 L_T : total ligand concentration
 $\overline{Z}_H$: proton formation function
 K_w : dissociation constant of water
 $\overline{Z}_M$: metal formation function
 β_j : thermodynamic formation constant of complex j
 E_{dc} : dc component of potential
 $\dot{E}_{ac}$: ac component of potential

- R : gas constant
- T : absolute temperature
- F : Faraday constant
- n : stoichiometric number of electron involved in an electrode reaction

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Chapter 1: Introduction

Chromium is a steel-grey metallic element naturally found in rocks, soil, animals, and in volcanic dust and gases. It has three main forms: Cr^0 , Cr^{III} and Cr^{VI} , the last two being the most important. In very small amounts, Cr^{III} is an essential nutrient in our diet. It is believed to help insulin maintain normal glucose and cholesterol levels, and enhance fat metabolism. Both Cr^{III} and Cr^{VI} are used for:

- i) making steel and other alloys,
- ii) bricks in furnaces,
- iii) dyes and pigments,
- iv) chrome plating,
- v) leather tanning,
- vi) wood preserving.

All forms of chromium can be toxic at high levels, but Cr^{VI} shows very high toxicity. Breathing very high levels of Cr^{VI} or for very long periods of time can irritate the nose, lungs, stomach and intestines. People who are allergic to it may also have asthma attacks after breathing high levels of either the (VI) or the (III) form. Ingesting very large amounts of chromium can cause stomach upset and ulcers,

convulsions, kidney and liver damage, and even death. Skin contact with liquids or solids containing Cr^{VI} may lead to allergic reactions including severe redness and swelling or even skin ulcers [1].

Cr^{III} is required for maintenance of proper carbohydrate and lipid metabolism; however, elucidating its function at a molecular level has proved to be problematic. Recent research has revealed that the chromium-binding oligopeptide chromodulin may play a unique role in the autoamplification of insulin signaling [2-8]. Over four decades ago, Walter Mertz and co-workers [9,10] demonstrated that chromium was an essential trace element for mammals. Rats that were on a specific diet, which proved to be chromium deficient developed an inability to respond efficiently to increases in blood glucose. The dietary factor necessary to prevent this glucose intolerance was named glucose tolerance factor (GTF) [9].

The inactive form of insulin receptor (IR) is converted to the active form by binding insulin (I) - see Figure 1.1. This triggers a movement of chromium from the blood into insulin-dependent cells, which in turn results in apochromodulin (pink triangle) binding chromium. Finally, the holochromodulin (green oval)

binds to insulin receptor, further activating the receptor kinase activity. Apochromodulin is unable to bind to receptor and activate kinase activity. When the insulin concentration drops, holochromodulin is released from the cell to relieve its effects [2].

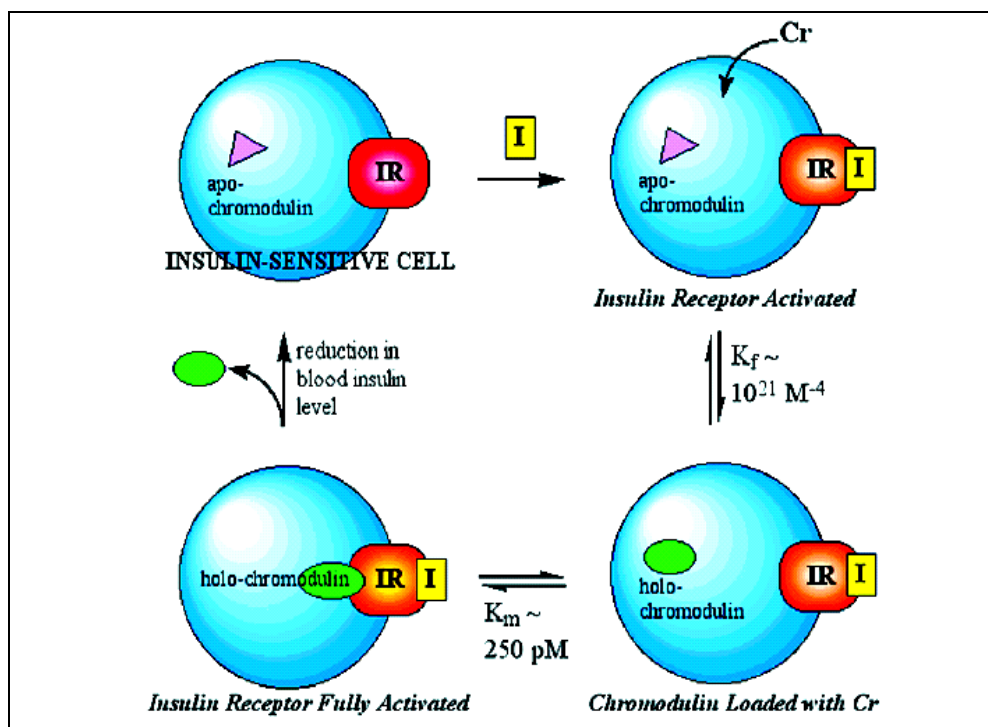


Figure 1.1: Proposed mechanism for the activation of insulin receptor activity by chromodulin (LMWCr) in response to insulin. Taken from [2].

Cr^{VI} is known for its high toxicity and was classified as a carcinogenic species. The oxidative damage to DNA nucleobases has been implicated in the etiology of cancers promoted by a wide variety of carcinogens [11,12]. A significant body of evidence exists for the interaction of Cr^{VI} with guanine nucleotides in DNA, including an enhanced chromium association with high-G-

content DNA [13], polymerase arrest at G-nucleotides [14,15], and oxidative damage centered at guanine sites [16,17]. Once internalized, Cr^{VI} is rapidly reduced to the ultimate intracellularly stable oxidation state, Cr^{III} [18]. During this reduction process, intermediate high-valent oxidation states of chromium such as Cr^{V} are formed both *in vitro* and *in vivo* [19-22]. The oxidative DNA damage induced by chromate is thought to be derived directly from these high-valent metastable intermediates or indirectly through the formation of radical species [23].

High-valent chromium complexes designed to model, intracellular chromate reduction products have primarily used oxygen-ligated anionic complexes such as the readily synthesized Cr^{V} -ehba complex. This complex was first shown to cause oxidative DNA damage by relaxation of supercoiled plasmid DNA [14]. Other model Cr^{V} complexes have also shown a preference for oxidation occurring at the deoxyribose sugar [18]. However, no model high-valent chromium complex has yet shown convincing interactions with the DNA nucleobases.

1.1. Chromium in water

Dissolved Cr is a trace element in uncontaminated waters, ranging in concentration from 0.05 µg/L in seawater [26] to about 500 µg/L in groundwater draining ultramafic rocks in regions with dry climates [27]. The highest known Cr concentration not resulting from human activity, about 7.5 mg/L, occurs in pH 12.5 groundwater near Maqarin, Jordan [28]. Contamination of groundwater with Cr as a result of human activity is widespread and persistent [29-31].

Chromium aqueous geochemistry has been reviewed recently by Richard and Bourg [32], who discussed conditions under which Cr may form aqueous organic and inorganic complexes, dissolve or precipitate, undergo redox transformations, and exhibit adsorption-desorption behavior. The authors concluded that mobility of Cr is determined by the competition between these above mechanisms and that Cr^{III} is mobile under acidic conditions or as dissolved organic complexes. Mobility of Cr^{VI} is significantly reduced in the presence of Fe^{II} or organic material [32].

Chromium reactions in seawater have been studied by Elderfield [33], Nakayama et al [34-36], Turner et al [37] and Pettine and Millero [38]. Elderfield [33] examined Cr speciation by both calculation and analysis and concluded that the thermodynamically favored Cr species are not found by analysis of seawater and that the predominant Cr^{III} species should be $\text{Cr}(\text{OH})^{2+}$. Nakayama et al [34-36] tested the hypothesis that most of the apparent discrepancies in valence species distribution of Cr in seawater are the result of complexing of Cr^{III} by naturally occurring organic materials. These authors proposed a method for determining the quantities of Cr in organic and inorganic complexes. Turner et al [37] examined the periodic nature of complexation of 58 elements considered trace constituents of seawater and concluded that the elements can be grouped according to their interactions with the predominant anionic ligands found in seawater. Pettine and Millero [38] determined the kinetics of oxidation of Cr^{III} to Cr^{VI} with respect to pH and concentration of H_2O_2 . In the absence of elevated concentrations of complexing anions, the predominant forms of dissolved Cr^{III} are $\text{Cr}(\text{OH})_{3(\text{aq})}^0$ at neutral pH, $\text{Cr}(\text{OH})_{(\text{aq})}^{2+}$ at more acidic pH, and $\text{Cr}(\text{OH})_{4(\text{aq})}^-$

in the alkaline pH region [39]. Similarly, the predominant forms of dissolved hexavalent Cr are $Cr_2O_7^{2-}_{(aq)}$ and $HCrO_4^{-}_{(aq)}$ below pH 6.5, and $CrO_4^{2-}_{(aq)}$ at alkaline pH [40].

A pE-pH diagram [41, 42] of aqueous inorganic Cr hydrolysis species based on the results of Ball and Nordstorm study [43] is shown in Figure 1.2. The right-hand ordinate shows the corresponding Eh scale (EMF based on the standard hydrogen electrode [44]). At a given temperature, Eh and pe differ by a constant [at 298.15 K, $pE = Eh(V) \times 16.903$]. There are no stability fields for aqueous Cr^{II} species within the stability field for $H_2O_{(l)}$. Chromium can change redox state in the redox range found in natural waters and is reduced from the hexavalent state CrO_4^{2-} , a soluble form, to the less soluble trivalent state, which readily forms oxide and hydroxide precipitates [45,46] and adsorbs to the surface of clay minerals [46-48]. At pH values greater than 4, Cr^{VI} is significantly more soluble than trivalent Cr^{III} .

Most of the Cr^{III} in surface waters eventually settles into sediments. Cr^{VI} tends to remain in solution due to its high water solubility and resistance to adsorption

until it is eventually reduced to Cr^{III} by organic matter present in the water [1,50].

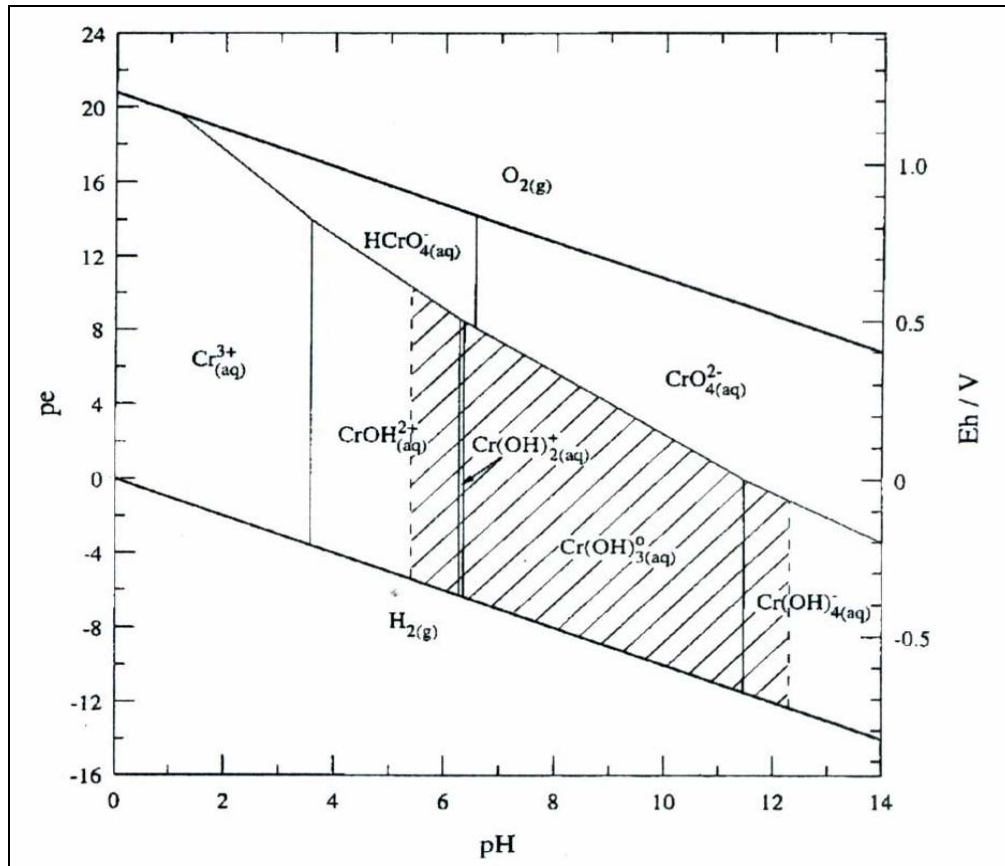


Figure 1.2: pE-pH diagram for aqueous inorganic chromium hydrolysis species (Cr^{III} data, [39]; Cr^{VI} data, [40]; redox data, [49]). Hatched area indicates predominance region for Cr(OH)_3 at $[\text{Cr}] = 1 \times 10^{-6} \text{ M}$. Taken from [43]

1.2. Chromium in ground

The average concentration of Cr in the earth's crust is about 100 $\mu\text{g/g}$. Average Cr concentrations in basaltic and ultramafic rocks are 200 and 2400 $\mu\text{g/g}$, respectively [50]. Chromium is one of the most common metal contaminants in soils because of its use in metal

plating, tanneries, wood preservation, and pigmentation [51,52].

Cr in uncontaminated soils is found as Cr^{III} and high proportions of Cr^{VI} are largely restricted to contaminated sites. Cr^{VI} transport and reduction in such contaminated soils ultimately reflects interdependent influences of physical, geochemical, and microbial processes. Prior to reduction, Cr^{VI} entering a soil may remain in solution, adsorb onto solid surfaces, or precipitate. Like other oxyanions, retardation of Cr^{VI} transport by adsorption is strongly pH dependent and weak under alkaline conditions [53].

A number of abiotic reactions may be responsible for the transformation of Cr^{VI} to Cr^{III} in soils. In soil solutions, Fe^{II} , S^{II} , and various organic compounds including fulvic and humic acids have been shown to reduce Cr^{VI} [54-58]. Reduction of Cr^{VI} on surfaces of Fe^{II} solids (Biotite, Fe^{II} impurities in $\alpha\text{-FeOOH}$, FeS , Magnetite, Ilmenite and green rusts) has been investigated [59-65]. Common soil minerals such as TiO_2 , Al_2O_3 , FeOOH , Montmorillonite, and Kaolinite have been shown to catalyze Cr^{VI} redox reactions with organic compounds and Fe^{II} [66-68].

Microorganisms can reduce Cr^{VI} in soil by both direct and indirect mechanisms. Indirect microbial Cr reduction proceeds through depletion of oxygen, reduction of Iron and Sulfur [69,70], and production of organic ligands and reductants. Direct microbial enzymatic reduction of Cr^{VI} in soils has also been reported [71-73]. A comparison of abiotic versus enzymatic Cr^{VI} reduction kinetics indicates that the abiotic pathways are expected to be dominant in most soils under reducing conditions [74]. Nonetheless, soil biological influences are expected to remain dominant, through promoting the indirectly microbial Cr reduction processes mentioned above.

1.3. Chromium in air

The chromium chemistry in the atmosphere resembles that in aqueous systems with precipitation, complexation and redox reactions influencing the abundance and ratio of the Cr forms [75]. Chromium is primarily removed from the air by fallout and precipitation. Thereafter it predominantly enters surface water or soil. Prior to deposition however, chromium particles of small size may remain airborne for long periods of time allowing them to be transported over long distances.

1.4. Chemical speciation

Chemical speciation analysis of an element yields information on the individual concentrations of the various chemical forms and phases in which an element exists in environmental samples. It allows for differentiation between oxidation states but also between simple and coordinated ions; cationic, neutral and anionic forms, protonated and unprotonated, monomeric and polymeric species, as well as between various degrees of homogeneous associations with natural constituents [75].

IUPAC defines this term as the state of distribution of an element among its possible different chemical forms and phases in a given matrix [76]. Basically there are two types of speciation, chemical speciation and physical speciation or fractionation. It is possible to distinguish four main types of chemical speciation analysis (Figure 3):

- i) Distribution speciation,
- ii) Isotopic speciation
- iii) Redox speciation,
- iv) Screening speciation.

The fractionation allows for the understanding of sorption and migration phenomenon of heavy metals in terrestrial systems (soil ↔ water) [75].

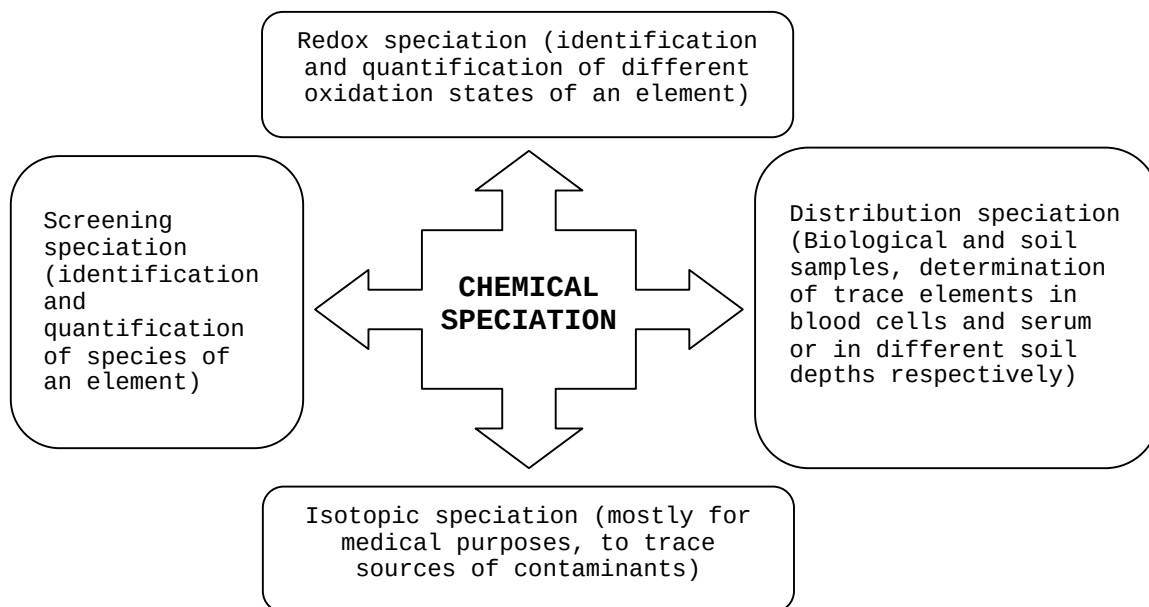


Figure 1.3: Classes of chemical speciation. Taken from [75]

1.5. Literature review

Considerable interest has developed in the determination and most importantly in speciation of two oxidation states (III and VI) of chromium in environmental, industrial and clinical samples. Electroanalytical techniques, particularly Adsorptive Stripping Voltammetry (AdSV) have been developed for measuring chromium at ultra trace level. i.e. ppt level [77-99]. For this purpose, the adsorptive collection of complexes of Cr^{III} with 2, 2' Bipyridyl (Bpy) [84-87], Cupferron [88], Diaminocyclohexanetetraacetic acid

(CDTA) [89], Ethylenediaminetetraacetic acid (EDTA) [89], Diethylenetriaminepentaacetic acid (DTPA) [77-83,92-99] and Diphenylcarbazide (DPCI) [90-92] at the working electrode surface is followed by voltammetric measurements of the adsorbed complex. All reported procedures are based on the determination of Cr^{III} complexes, because Cr^{VI} does not form complexes with any ligand. It must prior be reduced to Cr^{III} at -0.050 mV and then be complexed by a ligand.

Gao and Siow [84] have developed a catalytic adsorptive procedure using Bpy. As reported the method was for total chromium determination because an identical voltammetric response was observed for both Cr^{VI} and Cr^{III} . From all the reported metal ions only Ni and Co at concentration of about $0.10 \mu\text{M}$ and 15 nM interfere severely with the reduction peak of 2 nM of Chromium. Addition of $5.0 \mu\text{M}$ EDTA allowed to recover the reduction peak of chromium the detection limit was $2 \times 10^{-11} \text{ mol/L}$. *Korolczuk* [85,86] developed a method for determination and speciation of Cr^{VI} in the presence of large excess of Cr^{III} using Bpy. The method was based on the coprecipitation of Cr^{III} on aluminium hydroxide and then Cr^{VI} could be determined. $3 \times 10^{-9} \text{ mol/L}$ of Cr^{VI} was

not influenced by 10^{-6} mol/L of Zn^{II} , Fe^{III} , Pb^{II} , Cu^{II} , Ni^{II} , Mn^{II} , MnO_4^- , VO_3^- and MoO_4^{2-} . 1.0×10^{-7} mol/L of Co^{II} and 5×10^{-8} mol/L of Cr^{III} . Interference from surface active compounds was totally suppressed at more negative potential (-1.65 V). The detection limit was 4×10^{-11} mol/L. *Elleouet et al* [87] developed a method of chromium and copper determination using mixed ligands Bpy and oxime (8-hydroxyquinoline). That method has the advantage of the reduction in analysis time and the sample volume. As reported, interference could be caused by competitive adsorption of ions and their complexes onto the electrode. Copper reduction peak was not affected by addition of Pb^{II} , U^{VI} , Mo^{VI} and Sb^{III} at concentration down to 10^{-8} M/L. The reduction peak of 2×10^{-9} M of Cr was not affected by 3×10^{-8} M of Co and 5×10^{-8} M of Ni. The detection limit was 1.2×10^{-10} mol/L for Cr and 1.3×10^{-9} mol/L for Cu.

Cupferron was used by *Wang and Lu* [88]. They reported that Cr^{III} -cupferron complexes are more stable in time than Cr^{III} -DTPA complex used for the determination. This method is applicable for total chromium determination because Cr^{VI} and Cr^{III} give identical stripping peaks in the presence of Cupferron. Interference from Fe^{III} ,

Cu^{II} , Pb^{II} , Ni^{II} , Sb^{III} , Cd^{II} , Ga^{III} , Ge^{IV} , W^{VI} , Te^{VI} , Mn^{II} , V^{V} and Mo^{VI} at 10^{-7} mol/L was not observed in the determination of 1.9×10^{-9} mol/L of chromium. Concentration of Zn^{II} more than 10^{-7} mol/L interfere with the determination of chromium. The detection limit was 1.9×10^{-11} mol/L.

CDTA, DTPA and EDTA were used by Zarebski [89] in different supporting electrolytes (KCl and KNO_3). According to Zarebski, DTPA and EDTA showed higher sensitivity when compared to CDTA. Highest sensitivity of determination was achieved by application of EDTA and DTPA in nitrate supporting electrolyte. Low concentration of Cr^{VI} could be determined in DTPA + KNO_3 because the DP peak recorded for Cr^{VI} was higher when compared with Cr^{III} even if the nitrate concentration was varied. This was due to the freshly reduced Cr^{III} from Cr^{VI} . The comparison of Cr^{III} signal in DTPA + KNO_3 and EDTA + KNO_3 does not present significant improvement. The increase of NO_3^- concentration leads to the deterioration of the DP peak. EDTA + KNO_3 offered additional possibility of determination of Cr^{III} in the presence of Cr^{VI} as Cr^{III} could be removed from the supporting electrolyte by coprecipitation with BaSO_4 .

DPCI was used by *Malakhova et al* [90] have studied adsorption and electrochemical transformations of the Cr^{III} complex with DPCO on a graphite electrode in aqueous solutions. As reported, electrochemical transformations of the complex in combination with the data on chemical oxidation of the complex disintegration products indicated that the ligand and not Cr^{III} participated in electrode processes. The degree of Cr^{III} oxidation was not changed at the anodic stage, and the cathodic stage took place over a potential interval that was insufficient for reduction of Cr^{III} . The adsorptive cathodic stripping method using a graphite electrode was developed for Cr^{VI} determination. The detection limit was 1.0×10^{-9} mol/L. *Elleouet et al* [91] proposed a more sensitive method involving DPCI for determination of Cr^{VI} at a HMDE. As reported interference from chloride ion above 20 mg/L caused a total disappearance of the peak of chromium complex. Molybdate may form mercury (I) salt covering the HMDE and may cause the decrease observed in the reduction peak of Cr^{III} -DPCO complex. Fluvic acids also caused a decrease in the peak due to a competitive adsorption between fulvic substances and the complex or to the reduction of Cr^{VI} by fulvic acids. The detection

limit was 3.8×10^{-8} mol/l. *Paniaga et al* [92] to generate a diphenylcarbazide-modified carbon paste electrode that improves sensitivity of the analytical determination of Cr^{III} and Cr^{VI} . The procedure has lower sensitivity for Cr^{III} . The modification of the electrode was carried out to determine Cr^{VI} and Cr^{III} in order to carry out the speciation of the two oxidation states. As reported only Cr^{VI} react with DPCI and to give DPCO. Cr^{III} does not form complex with DPCO or DPCI. The method reported was based on the measurement of Cr^{VI} using the diphenylcarbazide-modified carbon paste electrode (DMCPE), oxidizing Cr^{III} to Cr^{VI} , determining the total chromium and Cr^{III} by subtraction.

DTPA was used by *Lanza and Taddia* [93] developed a sensitive method of Chromium determination in Gallium Arsenide using DTPA. Fast digital integrated circuits, low and high-power field effect transistors are often made on semi-insulating Gallium Arsenide substrates. Chromium is a common dopant for this material. The range of chromium content in semi-insulating Gallium Arsenide extends from about 1-2 ng/g for undoped material to 2-10 $\mu\text{g/g}$ in the chromium doped material. After sample pretreatment to convert Cr^{III} to Cr^{VI} , as

reported chromium could be determined at levels as low as 1 µg/g. As Gallium forms very stable complexes with DTPA, a large excess of DTPA was needed. Golimowski *et al* [94] who developed a method to determine total chromium in natural waters. The procedure was based on the preconcentration of Cr^{III}-DTPA complex by adsorption at the hanging mercury drop electrode. As reported the catalytic action of nitrate and bromate ions was elucidated using CV. The adsorption of chromium complexes at the HMDE was investigated by use of ACV. Interference from Pb^{II}, Cd^{II}, Cu^{II}, Fe^{II} and Mn^{II} at concentration of 1 mg/L was negligible. The detection limit was 2×10^{-8} mol/L. Boussemart *et al* [95] proposed a method of determination and speciation of chromium in sea water. Comparison of the chemical speciation of DTPA in sea water and distilled water indicated that the sensitivity for the procedure for Cr^{VI} in sea water was ten times lower than in distilled water. This was due to competing ions such as calcium and magnesium for DTPA in the sea water. Cr^{VI} produces a stable peak whereas the peak due to Cr^{III} was unstable due to probable conversion of the Cr^{III}-DTPA complex to an electrochemically inert complex over a period of 30 minutes. The interference by surface active compounds

was less by lowering the deposition time. It was also eliminated by UV-irradiation of the sample. Other metal could interfere if they form adsorptive complex with a reduction peak near that for chromium. The detection limit was 1.0×10^{-10} mol/L in sea water and 1.0×10^{-11} mol/L in fresh water. *Korolczuk and Grabarczyk* [96] developed a procedure for Cr^{VI} determination in flow system free from the interference of surface active compounds. The procedure consisted in four steps. i) reduction of Cr^{VI} to the metallic state onto the electrode, ii) oxidation of Cr^0 to Cr^{III} with formation of $\text{Cr}(\text{OH})_3$ adsorbed onto the electrode, iii) complexation of chromium hydroxide by DTPA and iv) reduction of Cr^{III} -DTPA complex in the presence of nitrates. Interference from other ions was carried out with a fixed Cr^{VI} concentration (1.0×10^{-8} M) Cr^{III} up to 1.0×10^{-6} M do not affect Cr^{VI} , addition of 1.0×10^{-2} M/L of MgSO_4 and CaCl_2 does also not influenced the peak of Cr^{VI} contrary to the method employing the adsorption of Cr^{III} -DTPA where a decrease in sensitivity near one order of magnitude was observed. The detection limit was 3×10^{-10} mol/L for Cr^{VI} concentration of 1.0×10^{-8} mol/L and 3.0×10^{-11} mol/L for Cr^{VI} concentration of 3.0×10^{-10} mol/L. *Cukrowska and Dube* [97] optimized an

analytical procedure for determination and speciation of Chromium using DTPA. As reported, their procedure was used for analysis of industrial waste, natural waters and soils. Interference from SO_4^{2-} (up to 5.0 g/L) and Cl^- (up to 1.0 g/L) showed no effect on chromium peak. The detection limit was 2.0×10^{-10} mol/L.

1.6. Research objectives

This work aims primarily at understanding the processes involved in the determination of Cr^{III} by AdCSV using Bpy as case study. Results so obtained will allow researchers to formulate the general requirements of Cr^{III} and Cr^{VI} speciation and determination by electro-analytical techniques.

- To investigate the complexation chemistry of Cr^{III} with Bpy by Glass Electrode Potentiometry (GEP) and Voltammetry.

- To elucidate the speciation model for Cr^{III} using Bpy as a ligand, that allows for the determination of complex stability constants.

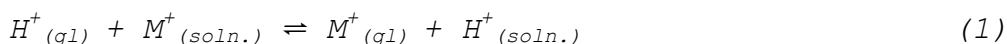
➤ To comment on the reversibility and/or reduction process of the Cr^{III} -Bpy systems including any adsorption phenomena occurring at the electrode surface.

Chapter 2: Review of some analytical methods

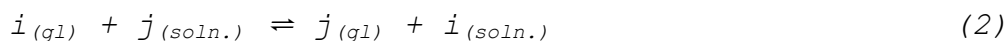
2.1. Potentiometric techniques

2.1.1. Glass Electrode Potentiometry

In the potentiometric method the emf between an indicator electrode and a reference electrode is measured, and the potential of the indicator electrode deduced [100]. In the region where the pH response is error-free, the only electrochemical process of concern is the exchange of protons between the solution and the gel layer in the hydrated glass surface. The potential E_g then follows the Nernst formula for the hydrogen electrode, although the standard potential is, of course, not usually zero. There is a corresponding alteration of the exchange equilibrium at the glass surface, with cations M^+ replacing some of the hydrogen ions occupying stable sites in the glass phase [101]:



or, in the general case,



With certain assumptions having to do with the number of exchange sites available to the two cations in the glass surface membrane and with the activity

coefficients of ions in the glass, Nicolsky [101] was able to derive the equation

$$E_g = \text{const.} + \frac{RT}{F} \ln(a_i + K' a_j) \quad (3)$$

E_g : potential of the glass electrode

$a_{i,j}$: activity coefficient of ions in the glass i and the solution j

where the constant K' was identified with the equilibrium constant K_{ij} for the exchange process described by Equation (2).

Although Nicolsky's equation was moderately successful in describing the change in potential of the glass electrode in mixtures of cations i and j , Eisenman, Rudin and Casby [101] found it possible to represent a wider range of experimental data by an equation of the form

$$E_g = \text{const} + \frac{nRT}{F} \ln\left(a_i^{1/n} + (K' a_j)^{1/n}\right) \quad (4)$$

In equation (4), K' and n are empirical parameters characteristic of the pair of ions and the composition of the glass. Theoretical studies now support the form of equation (4). It has been demonstrated that the voltage response of the glass electrode is to be regarded as the sum of two terms:

$$E_g = E_{ex} + E_d \quad (5)$$

namely the ion-exchange potential E_{ex} and a diffusion potential E_d .

2.1.2. Determination of stability constants

Stability constants for complexes can be determined by the use of glass electrode potentiometry. Let us assume a system given by the equation below



in which M represents the metal ion, L the ligand and H either a proton or an hydroxide ion.

At equilibrium in aqueous solution of a given pH, many complexes will exist. It is important to identify the complexes that exist in the solution and to determine their stability constants. This is readily achieved by glass electrode potentiometry.

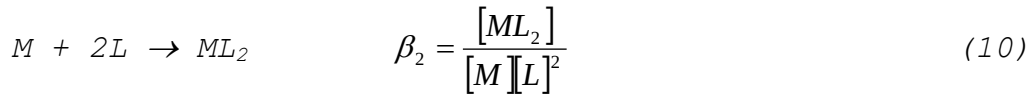
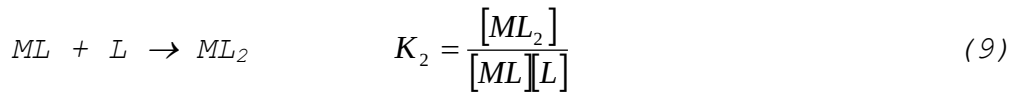
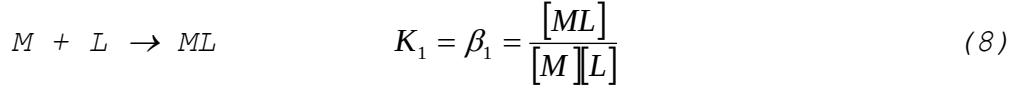
The formation of complexes ML_n from a metal M and n ligands L may be represented by an overall stability constant β_n that combines the corresponding stepwise stability constants K_n [102].

The potential developed at the indicator electrode depends on the activities of the species present in the solution. The use of a relatively large excess of an inert supporting electrolyte is therefore required [103, 104].

Overall stability constant for reaction described by Equation (6) is defined as

$$\beta_{pqr} = \frac{[M_p L_q H_r]}{[M]^p [L]^q [H]^r} \quad (7)$$

If we describe the stepwise equilibria as follow;



then from the equation above $\beta_2 = K_1 \times K_2$ and β_n can be expressed generally as

$$\beta_n = \prod K_n \quad (11)$$

The interpretation of the Potentiometric data is attained with the help of useful software packages. The raw data are obtained in the form of titrant volume and electrode potential. The Nernst equation is used to obtain the sensors potential E , where the glass electrode is the sensors for the free hydrogen ions in solution [100].

$$E = E^\circ - H_{slope} \times pH \quad (12)$$

Where E° is the electrode constant, H_{slope} is the electrode response slope and the pH is the negative logarithm of the free hydrogen ion activity or

concentration if experiments are performed at constant ionic strength.

2.1.3. Potentiometric data treatment

The data was analyzed using ESTA (Equilibrium Simulation and Titration Analysis) program [105]. ESTA is a computer program library (a collection of programs and subprograms) that performs calculations concerned with competitive aqueous solution equilibria.

ESTA has the capacity to accommodate chemical systems consisting of as many as 10 components forming up to 99 complexes. Titrations involving up to three electrodes and three burettes are permitted. The programs can take into account variations in ionic strength and the associated changes in activity coefficients. It also permits corrections of titration data affected by liquid-junction potentials and imperfect ion-selectivity of electrodes.

The ESTA library contains the following program modules, many of which perform more than one kind of calculation.

ESTA 1: The Simulation Module

By setting up and solving the mass balance equations, ESTA1 can determine, on a point-by-point basis, single values for almost any titration parameter. The calculations fall into two categories:

- Species-distribution calculations, specified by the task SPEC
- Potentiometric calculations including the determination of emf values (task SIME), formation constant estimates (task BETA), total analytical concentrations (task TOTL), initial vessel concentrations (task VESL) and initial burette concentrations (task BURT).

Other kinds of titration analysis are also possible; at each point the following can be obtained:

- percentage distributions of species for both SIME- and SIMV-type calculations (task ERR%)
- formation function values (task ZBAR)
- deprotonation function values (task QBAR), and
- appropriate weights, on overall objective function value and the relative contributions of the most important errors based on residuals in both emf and total concentrations (tasks OBJE and OBJT respectively)

ESTA 2: The Optimization Modules

There are two optimization programs, *ESTA2A* and *ESTA2B*, differing only in the way the weights are calculated. They are used when it is desired to determine, for one or more parameters, the best values, based on a least-squares procedure applied to a whole system of titrations.

The following parameters can thus be refined: formation constants, vessel and burette concentrations, electrode intercept, electrode slope and initial vessel volume.

It is possible to group together, over any combination of titrations local parameters of the same type and with the same value so that they are refined together as a single parameter. The objective function may be weighted or unweighted. The sum of squares of residuals may be minimized with respect to either emf-task OBJE or total concentrations-task OBJT.

The total number of titration is dimensioned to 20 and the total number of points to 1000.

A file of simulated titration data, with a format identical to ESTA input, can be generated as output [106].

During the speciation calculations, the conditions of mass balance are imposed by ESTA in the standard way by equating the calculated total concentration T_i^c with the real (analytical) concentration T_i^r .

$$T_i^r = T_i^c = [X_i] + \sum_{j=1}^{NJ} r_{ji} \Gamma_j \beta_j \prod_{n=1}^{NC} [X_n]^{r_{jn}} = \frac{C_i^v \times V^0 + \sum_{m=1}^{NB} C_{im}^B \times V_m}{V^0 + \sum_{m=1}^{NB} V_m} \quad (13)$$

$$\Gamma_j = \frac{\left(\prod_{n=1}^{NC} \gamma_n^{r_{jn}} \right)}{\gamma_j} \quad (14)$$

where:

C_i^v = initial vessel concentration (component i)

C_{im}^B = burette m concentration (component i)

V_m = burette m titer volume

V^0 = initial vessel volume

NB = number of burettes

i = $1, \dots, NC$

NC = number of components appearing in complexes

In general, the equation relating the potential of an electrode to the activity of the electrode ion can be written in the form [107]:

$$E_k = E_k^0 + E_k^{IS} + E_k^{LJ} \quad (15)$$

$k = 1, 2, 3, \dots$

where:

E_k^0 = electrode intercept

E_k^{IS} = electrode selectivity

E_k^{LJ} = liquid junction potential

For the purpose of formation-constant determination,

E_k^{IS} is usually given by:

$$E_k^{IS} = S_k \log \gamma_k + S_k \log [X_k] \quad (16)$$

where:

S_k = the electrode response slope,

γ_k = activity coefficient of the electrode ion,

The Nicolsky equation (2) was modified to accommodate the effects of interfering ions, the following equation was proposed:

$$E_k^{IS} = S_k \log \left[\{X_k\}^{\frac{1}{\alpha}} + \sum \left(K_{ki} \{X_i\}^{\frac{Z_k}{Z_i}} \right)^{\frac{1}{\alpha}} \right] \quad (17)$$

where:

S_k = the electrode response slope,

K_{ki} = the selectivity coefficient of component i ,

α = an empirical parameter,

Z_i = the charge on species i .

The correction for liquid junction potential changes across the junction of different univalent electrolytes at constant ionic strength and is described by the Henderson equation [first term in the right hand side of Equation (19)]:

$$E_k^{LJ} = E_k^{LJ'} - E_k^{LJ_0} \quad (18)$$

$$E_k^{LJ} = \frac{-RT}{F} \times \frac{\sum_i \gamma_i^s \{S_i^s\} - \lambda_i^b \{S_i^b\}}{\sum_i Z_i (\lambda_i^s \{S_i^s\} - \lambda_i^b \{S_i^b\})} \times \ln \frac{\sum_i \lambda_i^s Z_i \{S_i^s\}}{\sum_i \lambda_i^b Z_i \{S_i^b\}} - E_k^{LJ_0} \quad (19)$$

where:

λ_i^s = is the ionic conductance of species i in the test solution for all components,

λ_i^b = the ionic conductance of species i in the bridge solution,

Z_i = is the charge on species i ,

$\{S_i^s\}$ = is the activity of species i in the test solution,

$\{S_i^b\}$ = is the activity of species i in the bridge solution

$E_k^{LJ_0}$ = the liquid junction between the bridge solution and a solution containing the bridge ions at the reference ionic strength.

2.1.4. Calculation of Formation Functions

Equations (13), (17) and (19) require “thermodynamic” values of the parameters $\beta_j, E_k^o, K_{ki}, \lambda_i^s$ and λ_i^b those that are defined with respect to a standard state based on reactions occurring at infinite dilution in water at zero ionic strength. However, it is established practice to work with conditional constants $(I_{\beta_j}, I_{E_k^o}, I_{K_{ki}}, I_{\lambda_i^s}, I_{\lambda_i^b})$ which refer to some other ionic strength (I). Such constants, therefore, need to be converted into the corresponding thermodynamic values in the following way:

$$\beta_j = \frac{I_{\beta_j}}{I_{\Gamma_j}} \quad (20)$$

The NC (number of components appearing in complexes) mass-balance equations (m.b.e), equation (13), can be, in principle, solved for any NC unknowns as long as all remaining parameters are known. A Newton-Raphson procedure is used to solve the m.b.e. These functions are only defined for ligand (LH), binary (MLH) and ternary (MLXH) systems. The glass electrode is regarded as having been calibrated as a hydrogen ion concentration probe [105]:

$$E_H = I_{E_H^o} + S_H \log H \quad (21)$$

The Protonation Formation Function

The proton formation function is defined as

$$\bar{Z}_H = \frac{H_T - H + OH}{L_T} \quad (22)$$

Where:

H_T = total hydrogen ion concentration,

L_T = total ligand concentration,

and $OH = \frac{K_w}{H}$, where OH is the hydroxide ion and K_w is

the dissociation constant of water.

$\bar{Z}_H$ is plotted against $pH = -\log[H]$. This equation is used to evaluate both the "observed" and "calculated" functions from E_k^{obs} and E_k^{calc} respectively [105].

In the absence of the metal ion, the proton formation

function becomes $\bar{Z}_H = \frac{[bound\ H]}{L_T}$ (23)

where:

$$[bound\ H] = H_T - H + OH = H_T - H + K_w H^{-1} \quad (24)$$

Equation (22) becomes:

$$\bar{Z}_H = \frac{H_T - H + K_w H^{-1}}{L_T} \quad (25)$$

H_T and L_T are known from the analytically determined concentrations and K_w from the literature.

As H is measured by glass electrode, $\bar{Z}_H$ can be calculated at a number of pH values. Then the protonation curve can be plotted for $\bar{Z}_H$ against pH. Such curves help in giving valuable information about the form of the ligand at a particular pH range.

The Metal Formation Function

The metal formation function is defined as

$$\bar{Z}_M = \frac{L_T - A \left(1 + \sum_n \beta_{LH_n} H^n \right)}{M_T} \quad (26)$$

where:

$$A = \frac{(H_T - H + OH)}{\left(\sum_n n \beta_{LH_n} H^n \right)} \quad (27)$$

and M_T = the total metal concentration.

$\bar{Z}_M$ is plotted against $pA = -\log A$. This equation is used to evaluate both the "observed" and "calculated" functions from E_k^{obs} and E_k^{calc} respectively [105]. $\bar{Z}_M$ function gives the average number of ligand bond to the metal ion.

2.2. Voltammetric techniques

The term voltammetry in electroanalytical chemistry refers to any method in which the dependence of the current on the electrode potential is measured [108]. Electrochemical techniques can be used to provide speciation information, redox state and half wave potential measurements. This can be applied to metals, non metals and organic compounds.

2.2.1. Stripping analysis

Stripping analysis is a method that includes a bulk electrolysis step to preconcentrate a substance from solution into the small volume of a mercury electrode (a hanging mercury drop or a thin Hg-film) or onto the surface of a working electrode. After this electro-deposition or accumulation step, the analyte being determined is either re-dissolved from the electrode (anodic stripping mode) or reduced (cathodic stripping mode) using a selected voltammetric technique (e.g. differential pulse, linear scan, normal pulse, square wave, or alternating current mode) [109].

Anodic Stripping Voltammetry (ASV)

In anodic stripping voltammetry species are reduced into or onto the working electrode (a hanging mercury drop or a thin Hg-film) and then re-dissolved from the electrode. During deposition the analyte is preconcentrated into or onto the working electrode and during stripping the potential is changed in the way to promote the oxidation. The current of the peak recorded is proportional to the concentration of the analyte, in the bulk of the solution.

Cathodic Stripping Voltammetry (CSV)

In cathodic stripping voltammetry, the analyte is accumulated on the working electrode by application of an appropriate deposition potential. During the stripping step the electrode potential is swept in the cathodic direction.

Adsorptive Stripping Voltammetry (AdSV)

The use of adsorptive stripping voltammetry permits convenient measurements of over two dozen trace metals that cannot be readily deposited (e.g. Cr, Al, U, Fe, Ti, V, Mo)[110]. Generally in adsorptive stripping

voltammetry the mechanism involves the formation a surface active complexes of the target metal (in presence of a suitable complexing ligand) followed by the interfacial accumulation of the complex onto the working electrode. Most procedures involve the reduction of the metal in the adsorbed complex during the negative scan direction and are particularly called cathodic adsorptive stripping voltammetry (CASV). The mechanism of adsorption was described by Wang et al [111] as:

- The metal M^{n+} reacts with a ligand L to form the complex in solution



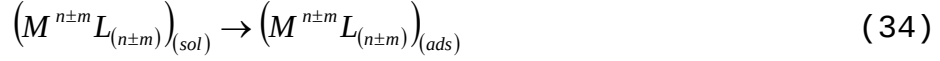
The complex is then adsorbed onto the electrode surface



- Alternatively, the ligand L is adsorbed first followed by the complexation reaction



- Metal cations do not always form a surface-active complex with the ligand; instead an oxidized or reduced electrochemical product of the metal cation forms such a complex.



Van den Berg [111] has reported that the stripping occurs via three mechanisms, reduction of the elemental species in the adsorbed complex, reduction of a ligand in adsorbed complex, and the catalytic evolution of hydrogen.

2.2.2. Alternating Current Voltammetry (ACV)

AC voltammetry is an extension of classical linear sweep techniques such cyclic voltammetry. Its main strength lies in the quantitative characterization of electrode processes and can also be used for analytical purposes [110]. AC voltammetry is basically a faradaic impedance technique in which the mean potential, E_{dc} , is imposed potentiostatically at arbitrary values that usually differ from the equilibrium value. E_{dc} is varied systematically on a long time scale compared to that of the superimposed AC variation, $\dot{E}_{ac}$ (10 Hz to 100 kHz). The output is a plot of magnitude of the AC component of the current versus E_{dc} . The phase angle

between the alternating current and $\dot{E}_{ac}$ of interest [112].

Treatments of this problem are greatly simplified by uncoupling the long-term diffusion due to E_{dc} from the rapid diffusional fluctuations due to $\dot{E}_{ac}$. We do that by recognizing that E_{dc} sets up mean surface concentrations that look like bulk values to the AC perturbation because of the difference in the time scale. The faradaic impedance is defined in terms of bulk concentrations; thus the current response in AC voltammetry as a function of E_{dc} is readily obtained by substituting the surface concentration imposed by E_{dc} directly into these impedance relations.

The mean surface concentrations enforced by E_{dc} depend on many factors [112]:

- the way in which E_{dc} is varied
- whether or not there is periodic renewal of the diffusion layer,
- the applicable current-potential characteristic,
- and homogeneous or heterogeneous chemical complications associated with the overall electrode reaction.

In the fundamental mode, one employs phase sensitive detection to measure the current component in phase with the excitation signal $\dot{E}_{ac}$. In contrast, the charging current is ideally 90° out of phase with $\dot{E}_{ac}$, since it passes through a purely capacitive element. It therefore has no projection in phase with $\dot{E}_{ac}$. Thus we expect the current in phase to be purely faradaic, whereas the current at 90° (the quadrature current) contains a second faradaic component plus the nonfaradaic contribution. By taking the current in phase as the analytical signal, we discriminate effectively against the capacitive interference [112].

In Figure 2.1, an AC voltammogram of n-pentanol in sodium nitrate is shown. From that Figure the adsorption process can be seen and interpreted by the appearance of an adsorption peak to more positive potential and a desorption peak to more negative potential.

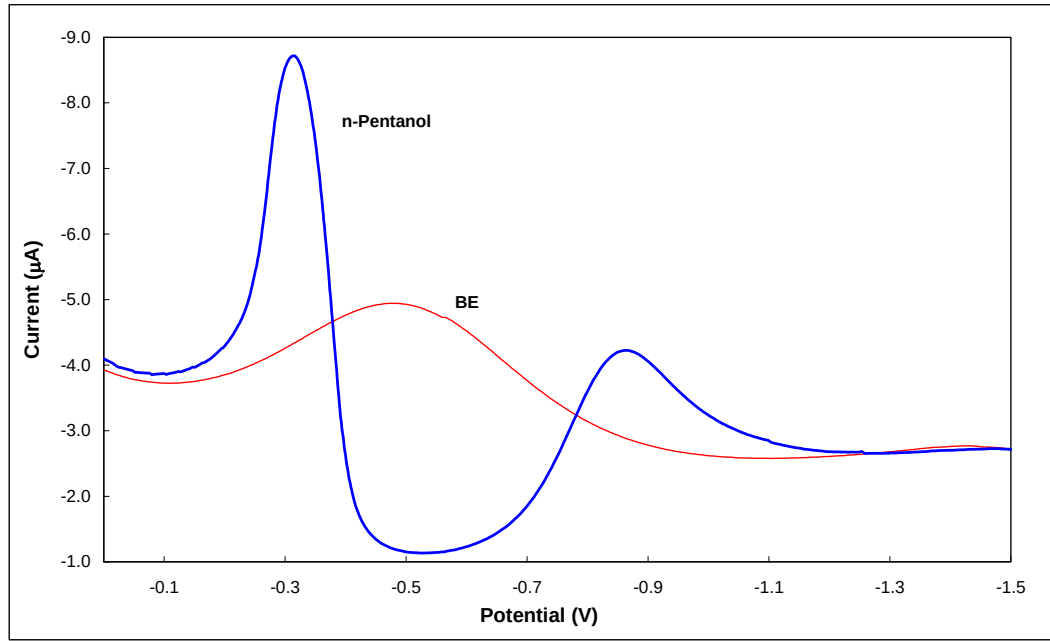


Figure 2.1: AC voltammogram of 3×10^{-2} M n-pentanol in 0.1 M sodium nitrate adjusted to pH 5.8. HMDE used as working electrode.

Capacitance Measurements

If C_0 is the capacitance of the electrolyte double layer in the absence of film formation and C the capacitance measured after an adsorbed film has formed, then in general $C < C_0$, since the presence of an adsorbed layer will increase the thickness of the double layer. Assuming that the decrease, $C - C_0$, is proportional to the coverage of adsorbed species, and that C_{min} is the measured capacitance for the case of maximum coverage, then:

$$\theta = \frac{C_0 - C}{C_0 - C_{min}} \quad (35)$$

Experimentally, the method is straightforward: the electrode surface must, as before, be cleaned and prepared in a reproducible state, and the capacitance measured by alternating current methods as described above [108].

2.2.3. Cyclic Voltammetry (CV)

Cyclic voltammetry involves the imposition of a triangular waveform as the potential on the working electrode, with the simultaneous measurement of the current. Negative and positive turn-round potentials, E_t^c and E_t^a are usually chosen in aqueous electrolyte to lie between the hydrogen and oxygen evolution potentials, which has the advantage that any adsorbed impurities that might otherwise block the electrode process of interest can be removed either by oxidation or reduction [108]. When interpreting a cyclic voltammogram one has to be careful as regards the exact direction of the individual scans.

Cyclic voltammetry has become a very popular technique for initial electrochemical studies of new systems and has proven very useful in obtaining information about complicated electrode reactions. It offers a number of

advantages in the treatment of linear sweep data. For a reversible reaction, the curves of $I(t)$ versus E for the forward and backward scans superimpose, with $I(t)$ returning to zero at sufficiently positive potentials. For a quasireversible reaction, however, the forward and backward $I(t)$ curves do not coincide. One can regard this effect as a consequence of the shifting of the E_{pc} and E_{pa} values from their reversible values [112]. In general, a perturbing chemical reaction can affect the primary measured parameter of the forward reaction (e.g. $E_{1/2}$ or E_p), and the reversal parameters (e.g. i_{pa}/i_{pc}). In Figure 2.2 can be seen the potential wave form and the representation of a CV voltammogram.

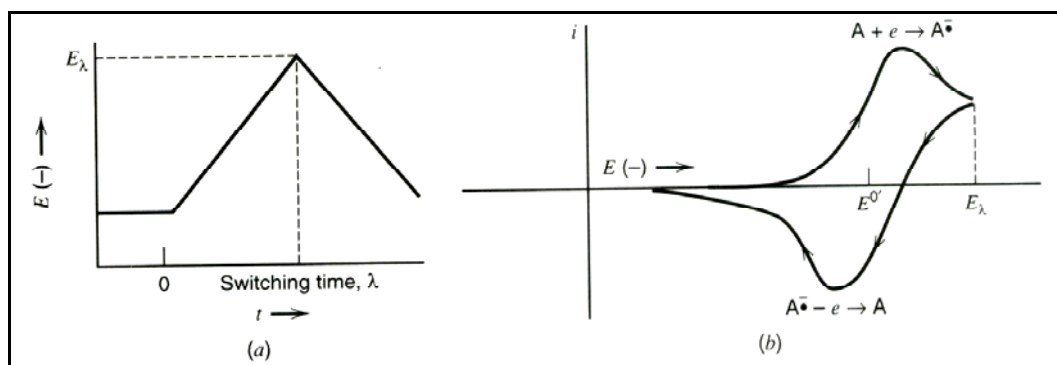


Figure 2.2: Potential wave form and schematic voltammogram for Cyclic voltammetry [taken from 112].

CV is not an ideal method for quantitative evaluation of system properties that must be derived from peak heights, such as concentration or the rate constant of a coupled homogenous reaction. The power of the method

lies in its diagnostic strength, which is derived from the ease of interpreting qualitative and semi-quantitative behavior. Once a system is understood mechanistically, other methods are often better suited for the precise evaluation of parameters. The difference between E_{pa} and E_{pc} , often symbolized by ΔE_p , is useful diagnostic test of a nernstian reaction. For one electron transfer process, it is always close to 59 mV and for a Quasireversible process it is at least 90 mV.

2.2.4. Differential Pulse Voltammetry (DPV)

The basis of all pulse techniques is the difference in the rate of the decay of the charging and the faradaic currents following a potential step (or "pulse"). The charging current decays exponentially, whereas the faradaic current (for a diffusion-controlled current) decays as a function of $\frac{1}{(t)^{1/2}}$; that is, the rate of decay of the charging current is considerably faster than the decay of the faradaic current. The charging current is negligible at a time of $5R_uC_{dl}$ after the potential step (R_uC_{dl} is the *time constant* for the electrochemical cell, and ranges from μs to ms) [113]. Therefore, after

this time, the measured current consists solely of the faradaic current; that is, measuring the current at the end of a potential pulse allows discrimination between the faradaic and charging currents.

The differential pulse techniques are among the most sensitive means for the direct evaluation of concentrations. In addition, they can provide information about the chemical form in which an analyte appears. Oxidation states can be defined; complexation can often be detected [112].

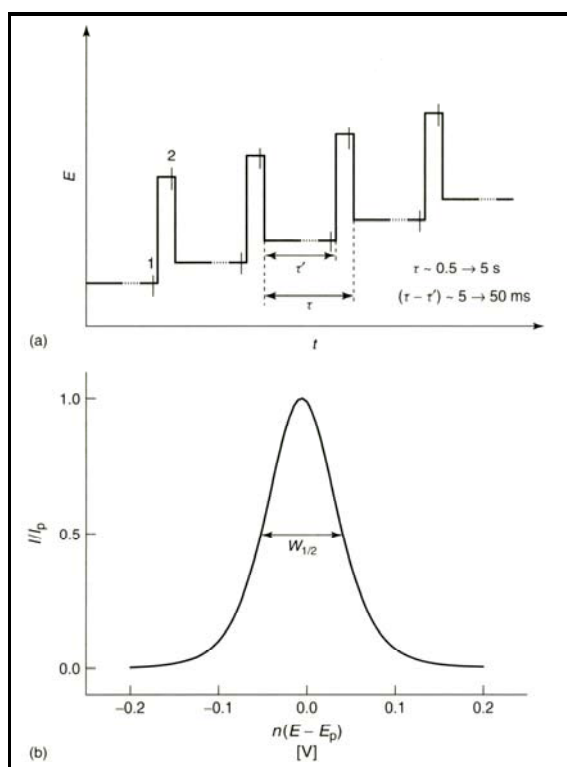


Figure 2.3: Potential wave form and schematic voltammogram for Differential Pulse Voltammetry [taken from 112]

Chapter 3: Experimental

3.1. Equipment

Potentiometric experiments were performed using a *Metrohm 809 Titrando* to determine protonation constant of Bpy and stability constants of Cr^{III} -Bpy complexes. Voltammetric experiments were performed using a *Metrohm 757 VA Computrace* equipped with a multi mode electrode model 6.1246.020. Differential Pulse Voltammetry (DPV), Cyclic Voltammetry (CV), and Alternating Current Voltammetry (ACV) were used. A hanging mercury drop electrode mode was selected in the determination operations. The automatic addition of auxiliary solutions was achieved with a use of *Metrohm 765 Dosimat* to avoid errors of manual pipetting. Finally, the measurements of pH were performed using a *Metrohm 713 pH Meter* connected to a glass electrode model 6.0234.100 (3 M KCl).

3.2. Reagents

All metal salt used were of analytical grade (A.R). No purification was performed. Deionized water used in the preparation of solutions was obtained by passing distilled water through a Milli-Q-water purification

system (Millipore, Bedford, MA, USA). The ligand 2, 2' bipyridyl ($C_{10}H_8N_2$, F.W. 156.19, 99% pure), chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$, F.W. 266.45, 99.995% pure), nickel chloride ($NiCl_2$, F.W. 129.62, 98% pure), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, F.W. 291.03, 98% pure) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, F.W. 297.48, 98% pure) were obtained from Sigma Aldrich. Sodium hydroxide (NaOH, F.W. 40.00, 98% pure) and sodium nitrate ($NaNO_3$, F.W. 84.99, 98% pure) were obtained from Saarchem (Muldersdrift, South Africa). Sodium nitrite ($NaNO_2$, F.W. 69.00, 98%), nitric acid (HNO_3 , F.W. 63.01, 65%), ammonia (NH_3 , F.W. 17.03, 25%), ammonium chloride (NH_4Cl , F.W. 53.49, 99.8% pure) and ethanol (C_2H_5OH , F.W. 46.07, 99.5%) were obtained from Merck (Darmstadt, Germany).

3.3. Preparation of solutions

The stock solutions of Cr^{III} , Co^{II} , Ni^{II} and, Zn^{II} were prepared by weighing the required mass of the metal salt using the *Precisa 180A* weighing balance. The salts were then dissolved in 0.01 M HNO_3 . All metal stock solutions were adjusted to 0.1 M ionic strength by adding $NaNO_3$. The ligand stock solution was obtained by dissolving the required mass in a solution of 0.09 M $NaNO_3$ and 0.01 M HNO_3 .

3.4. Glass Electrode Potentiometry

3.4.1. Determination of the protonation constant of Bpy

The determination of the protonation constant was performed by an automatic titrator (*Metrohm 809 Titrando*) using a combination glass electrode *Metrohm* model 6.0234.100 (Ag/AgCl 3 M KCl). The calibration of the glass electrode was performed with the use of acid-base titration. The procedure required an addition of a standard solution of NaOH to the cell containing the standard solution of HNO₃. All solutions were adjusted to 0.1 M ionic strength. Experiments were performed at 25 ± 0.1 °C. Next, 20 ml of 0.015 M stock solution of the ligand was pipetted in the cell using a *Metrohm* Dosimat 765. Additions of 0.1 ml aliquots of 0.02 M NaOH in 0.08 M NaNO₃ standard solution were maintained until neutral pH was reached.

Data points from potentiometric titrations were acquired with the following parameters:

- The volume increment for the titer (0.02 M NaOH) was set to 0.10 ml (The volume increment is the volume to be added at each dosing step. This must be well chosen if we want to reach high accuracy.)

- The signal drift was set to 0.5 mV per minute.
(The signal drift is the fluctuation in the measured value per minute that has to be met for measured value acceptance.)
- The minimum waiting time was 60 seconds. (The minimum waiting time is important for drift-controlled measurements. Measured value will be only accepted when the minimum waiting time has elapsed, even when the measured value drift has been achieved. The drift continues to be checked while the waiting time is elapsing.)
- The maximum waiting time was set to 120 seconds.
(If the measured value drift is switched off or has not yet been achieved then the measured value will be accepted after the maximum waiting time has elapsed.)

3.4.2. Determination of stability constants of Cr^{III} - Bpy

The titration of Cr^{III}-Bpy system was performed by mixing appropriate volumes of the stock solutions of Cr^{III} and Bpy to reach different L_T:M_T ratios. All solutions were adjusted to 0.1 M ionic strength. The L_T:M_T ratios used were 1.01, 2.02, 3.08, 4.05, and 9.18.

Data points were acquired using the following titration parameters:

- 0.1 ml volume increment of 0.02 M NaOH
- signal drift of 0.2 mV per minute
- minimum waiting time of 300 seconds
- maximum waiting time of 1500 seconds

Table 3.1: Specifications of the preparation of the sample for different $L_T:M_T$ ratios for data collected from pH 2 to pH 6.5

$L_T:M_T$ Ratio	Cr^{III} stock solution (ml)	Bpy stock solution (ml)
1	5	5
2	5	10
3	5	15
4	4	16
9	2	18

All titrations were stopped at around pH of 6 as the precipitation was found to occur soon after. The metal hydrolysis constants and pK_w were taken from the literature [113] and were held at fixed values during optimization and refinement procedures.

3.5. Voltammetry

The voltammetric experiments were performed by use of a Metrohm 757 VA Computrace equipped with a multi mode electrode model 6.1246.020. All experiments were performed at 25 ± 0.1 °C. A Metrohm 713 pH Meter together with a combination glass electrode model 6.0234.100 (Ag/AgCl 3 M KCl) were used to monitor pH.

The calibration of the glass electrode was done by use of Metrohm buffer solutions of pH 4 and pH 9. Deaeration of the sample solutions was performed with the use of high purity nitrogen. Three different voltammetric modes were used [Alternating Current Voltammetry, Cyclic Voltammetry and Differential Pulse Voltammetry].

3.5.1. Investigation of Adsorption Phenomena

Investigation of adsorption phenomena of Bpy ligand and Cr^{III} -Bpy complexes, on a hanging mercury drop electrode (HMDE) were performed by use of Alternating Current Voltammetry. The following parameters were selected: phase angle ($^{\circ}$): 90, frequency (Hz): 60, amplitude (Vrms): 20, modulation time (s): 0.050, voltage step time (s): 0.8, voltage step (V): 0.004, deposition potential (V): -1; deposition time (s): 30, equilibration time (s): 10 and initial purge time (s): 600.

3.5.2. Investigation of Electrochemical Reversibility

The Electrochemical Reversibility of reduction of Bpy ligand and Cr^{III} -Bpy complexes at the hanging mercury drop electrode (HMDE) was investigated by use of cyclic voltammetry. The following parameters were selected:

voltage step (V):0.004, sweep rate (V/s): 0.050, deposition potential (V): -1; deposition time (s): 30, equilibration time (s): 10 and initial purge time (s): 600.

3.5.3. Investigation of the Reduction Process

The reduction of Bpy ligand, and Cr^{III} -Bpy complexes on the hanging mercury drop electrode (HMDE) was performed by use of Differential Pulse Voltammetry. In this regard, the following parameters were selected: sweep rate (V/s): 0.010, pulse amplitude (V): 0.050, pulse time (s): 0.040, voltage step (V):0.004, deposition potential (V): -1; deposition time (s): 30, equilibration time (s): 10 and initial purge time (s): 600.

3.5.4. Experimental Procedure

The general procedure for all experiments can be summarized as follows:

- The combination glass electrode was calibrated prior to the voltammetric experiment using Metrohm buffer solutions of pH 4 and 9.
- The experimental vessel was cleaned with 0.05 M HNO_3 three times followed by thorough rinsing with deionized water.

- After the cleaning of the cell, 20 ml of 0.1 M of the background electrolyte was added to the cell and nitrogen was used to deaerate the solution.
- The purity of the background electrolyte was checked by recording the voltammogram on that solution.
- The required volume of the ligand stock solution (Bpy) was added to give the required total ligand concentration. After an additional deaeration of the sample a voltammogram was recorded.
- The required volume of the metal stock solution (Cr^{III}) was added, and after the deaeration time, a voltammogram was recorded.
- The pH of the solution was varied by adding the solutions of NaOH or HNO_3 .

Additional experiments involved a study of influence of the nitrate and the ligand concentration, the variation of deposition time, and the influence of interfering ions on the analytical signal.

- Nitrate concentration was varied to set the optimum condition for the catalytic effect.

- The ligand concentration and the deposition time were also varied to set the optimum values for a maximum peak height.
- The interfering ions were added to see their influences on the variation of the peak height of Cr^{III} -Bpy complexes.

Chapter 4: Results and discussion

4.1. Potentiometry

Glass electrode potentiometry (GEP) is the most established speciation technique (this technique accounts for over 80% [114] of all stability constants reported in literature and stability constants obtained from GEP might often be regarded as most reliable [115]).

4.1.1. Protonation constant

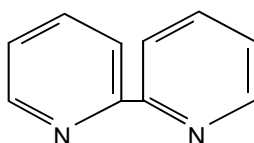


Figure 4.1: Structure of 2,2'-Bipyridyl

2,2'-Bipyridyl (Bpy) is a neutral ligand with two protonation constants $pK_1 = 4.54$ and $pK_2 = 1.50$ [116]. The first protonation constant of Bpy shown in Table 4.1 was redetermined in this work by glass electrode potentiometry (GEP) at an ionic strength of 0.1 M and 25° C.

Table 4.1: Protonation constant of Bpy established in this work at ionic strength 0.1 M sodium nitrate.

Cation	Equilibrium	Log K	Hamilton R-factor
H ⁺ (1 st titration)	H + L = HL	4.4746 (0.0003)	0.0016
H ⁺ (2 nd titration)	H + L = HL	4.4791 (0.0003)	0.0018
H ⁺ (3 rd titration)	H + L = HL	4.4931 (0.0011)	0.0068
H ⁺ (overall)	H + L = HL	4.4922 (0.0005)	0.0046

Only the first protonation constant located in the pH range around 4.5 was successfully determined. The second protonation constant remained inaccessible given the limitations of the glass electrode used in the adopted experimental procedure. The protonation potentiometric curve of Bpy versus pH is shown in Figure 4.2. The value 4.49 for pK_1 refined from the data generated in this study was used in the refinement operation for the modelling of Cr^{III}-Bpy complexes. From Figure 4.3, one can directly see that the deprotonated form (L) of the ligand is of major interest for the complexation of Cr^{III}. The second protonation constant is expected to occur at very low pH prior to the formation of a complex. All the voltammetric procedures involving this ligand in the determination of Cr^{III} are therefore performed at a higher pH range where the first protonation constant is influential.

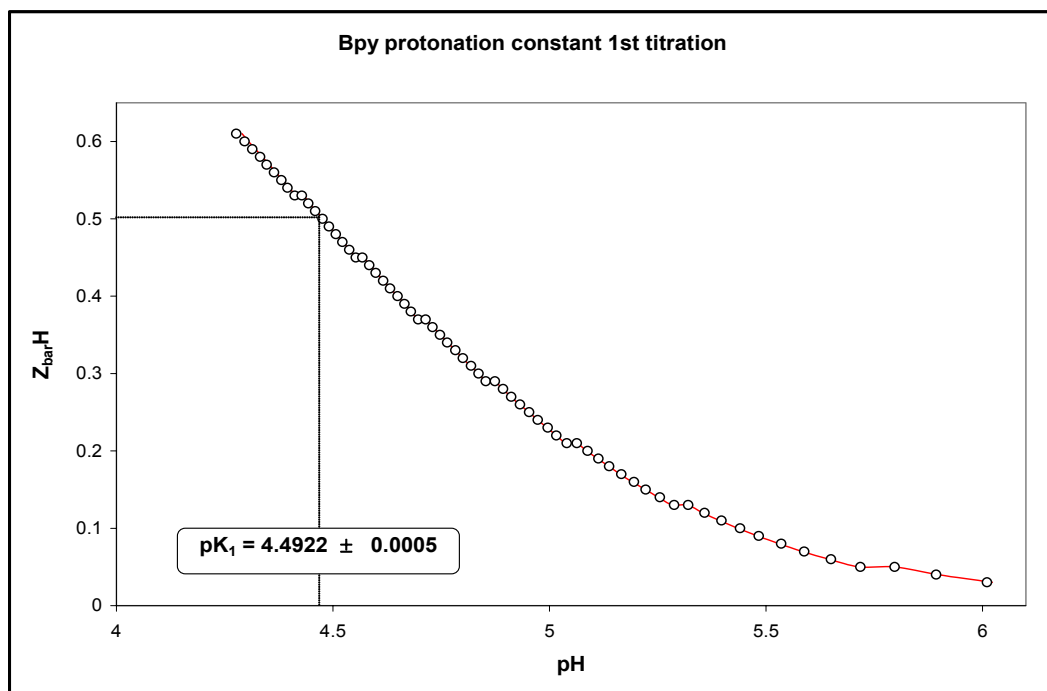


Figure 4.2: Experimental (circle) and theoretical (solid line) potentiometric protonation curve in the pH range between 4.3 and 6.0 for Bpy ligand studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T = 1.5 \times 10^{-2}$ M.

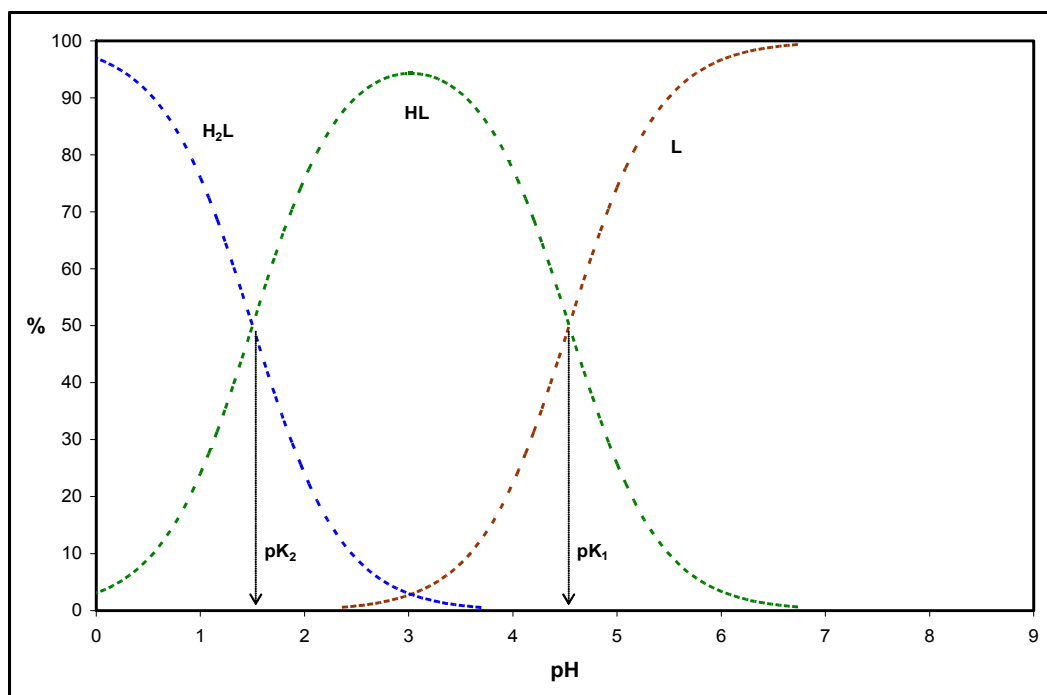


Figure 4.3: Bpy species distribution diagram plotted as a function of pH.

4.1.2. Potentiometric formation constants for Cr^{III}-Bpy species

The formation constants of Cr^{III}-Bpy species were established from five different L_T:M_T ratios (1.01, 2.02, 3.08, 4.05 and 9.18). The experiments were performed at 25 ± 0.1°C and at the ionic strength of 0.1 M in NaNO₃. The pK_w employed in this work was fixed at 13.78 [116]. As a result of the precipitation of Cr^{III}-Bpy complexes occurring approximately at pH 6, all titrations data was acquired in the interval 2.2 ≤ pH ≤ 6.5. According to the analysis of data collected for different L_T:M_T ratios (Figures 4.4-4.5) irregularities in the potentiometric curve may be evident from pH of 5. This is particularly true for L_T:M_T ratio 1. Increasing L_T:M_T ratio curtails precipitation and the irregularities referred to above occur at a higher pH. In general, the nature of the precipitation is such that it only becomes visible at pH ≈ 6.

This was taken into account during the refinement and all data points on the diagrams enclosed by ellipses were excluded from the refinement operation. In so doing one can successfully eliminate any changes of the initial metal total concentration in the cell, due to the precipitation that inevitably leads to inadequate

modelling of the data e.g., generating high standard deviations in the refined values of stability constants and relative high Hamilton R-factors.

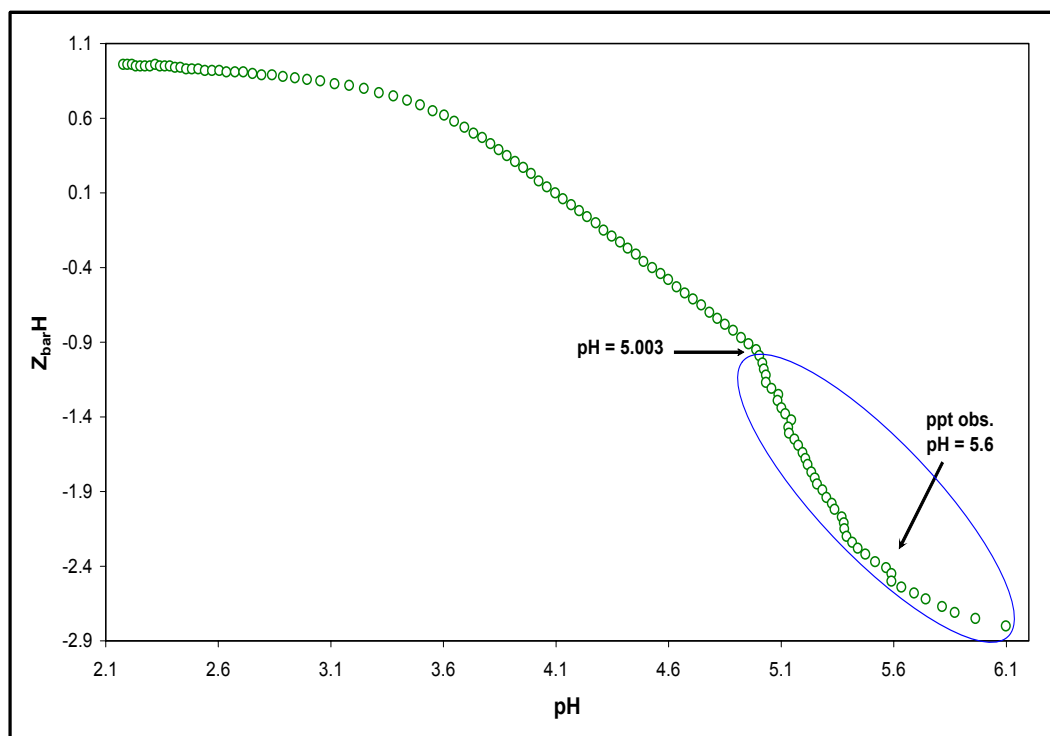


Figure 4.4: Experimental (circle) potentiometric protonation curve in the pH range between 2.1 and 6.1 for Cr^{III} -Bpy system studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T:M_T$ ratio 1 $L_T=5.1 \times 10^{-3}\text{M}$; $M_T=4.9 \times 10^{-3}\text{M}$.

The $\bar{Z}_H$ function seen in Figures 4.4-4.5 were generated by ESTA for M-L-H models that included ML, MLOH, $\text{ML}(\text{OH})_2$ and $\text{ML}(\text{OH})_3$. However, regardless on model tested, the last point as marked in Figures 4.4-4.5 were always out of the expected trend.

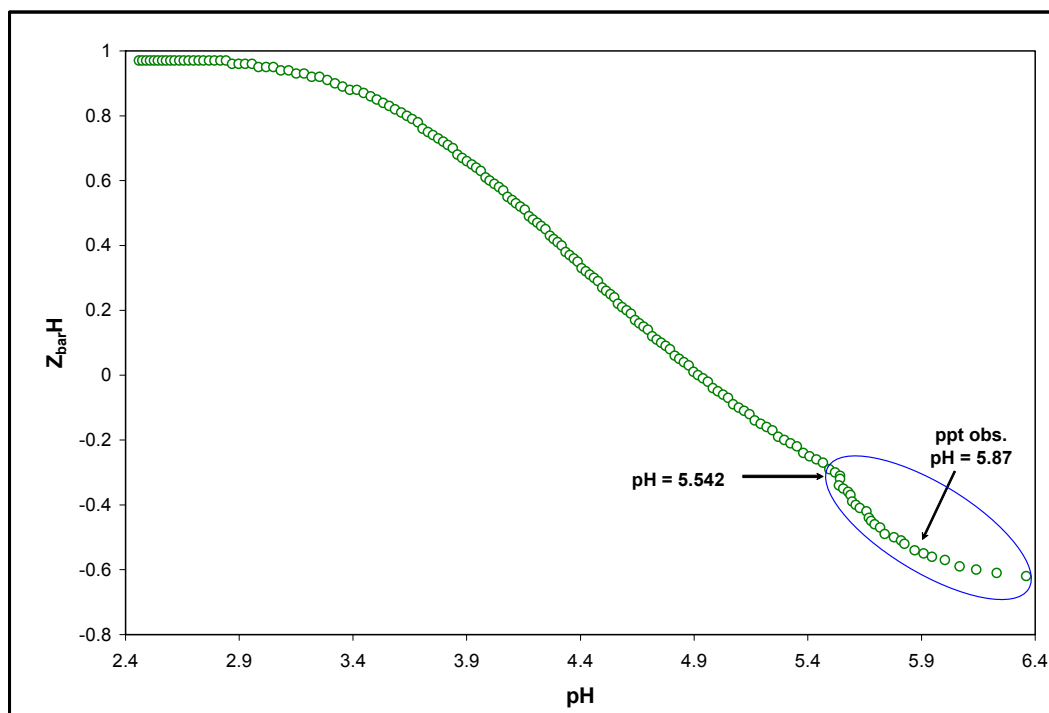


Figure 4.5: Experimental (circle) potentiometric protonation curve in the pH range between 2.5 and 6.4 for Cr^{III} -Bpy system studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T:M_T$ ratio 4 $L_T = 8.2 \times 10^{-3}\text{M}$; $M_T = 1.8 \times 10^{-3}\text{M}$.

Refinement of data

Different refinement operations of the potentiometric data were performed on the basis of thermodynamics data of chromium hydroxo species drawn from NIST critically selected stability constant of metal complexes database version 8 [116]. The following assumptions have been tested:

1. The formation of the chromium metal hydroxo species could be regarded as fast when compared with the time scale of GEP experiment. In this case, all known metal hydroxo species $\text{Cr}_x(\text{OH})_y$ were included in the refinement operation,

2. The kinetics of formation of some chromium metal hydroxo species might be assumed to be slow. In this case, all slowly formed metal hydroxo species were excluded from the refinement operation,
3. An assumption was made that the kinetics related to the formation of all metal hydroxo species of chromium is slow; all metal hydroxo species $\text{Cr}_x(\text{OH})_y$ were excluded from the refinement operation.

Refinement according the first assumption

The refinement operation was performed by including in the model all chromium hydroxo species seen in Table 4.2.

Table 4.2: Hydrolysis of aqueous inorganic chromium in sodium perchlorate at 25°C and ionic strength 0.1 M. Data from NIST critically selected stability constant of metal complexes database version 8 [116].

Species	Log β
CrOH	9.78
Cr(OH) ₂	17.30
Cr ₂ (OH) ₂	24.00
Cr ₃ (OH) ₄	37.00
Cr ₄ (OH) ₆	80.20

During the refinement operation, the following metal-ligand model ML and $\text{ML}(\text{OH})_3$ resulted in a very bad fit for both calculated, and experimental potentiometric $\bar{Z}_H$ and $\bar{Z}_M$ functions. Table 4.3 contains refined

values of the stability constants for metal complexes included in the model. The fitting of the experimental and theoretical functions can be seen in Figures 4.6-4.7. From these diagrams it is clear that the optimization for the suggested model is inadequate. The back-fanning feature on the $\bar{Z}_M$ curve (Figure 4.7) shows the formation of hydrolyzed chromium complexes. These hydrolyzed complexes are dominant in the solution and resulting in the earlier back-fanning behavior. The theoretical function (solid line) shows that complexes are formed instantaneously; the very first computed $\bar{Z}_M$ value is over 1. According to the experimental function (circles), it is clear that the formation function starts at $\bar{Z}_M$ value close to zero at almost one order of magnitude larger A value than that observed for theoretical function (solid line). This indicates that: (i) the complexation reaction is affected by slow kinetics (ii) the proposed model is wrong, (iii) the assumption made for that case, e.g., that the formation of all $\text{Cr}_x(\text{OH})_y$ was kinetically fast, was incorrect. This therefore does not allow for an optimized model of speciation including the mentioned chromium metal hydroxo species in the refinement.

This is further evidenced by the species distribution diagram plotted as a function of pH (Figure 4.8). It shows the competition between ML, $\text{Cr}_4(\text{OH})_6$ and $\text{ML}(\text{OH})_3$. ML is the dominant species from pH 1 to 4.5, where $\text{Cr}_4(\text{OH})_6$ becomes dominant up to pH 6. $\text{ML}(\text{OH})_3$ starts to be the major species above pH 6 and remains the only one complex in solution.

Table 4.3: Formation constants for chromium with Bpy found in this work at 25°C and ionic strength 0.1 M by glass electrode potentiometry (GEP) $L_T:M_T$ ratio 4. $L_T = 8.2 \times 10^{-3}\text{M}$, $M_T = 1.8 \times 10^{-3}\text{M}$. Values refined in the presence of all chromium hydroxo species.

Species	Log β
ML	6.55 ± 0.087
$\text{ML}(\text{OH})_3$	31.99 ± 0.207

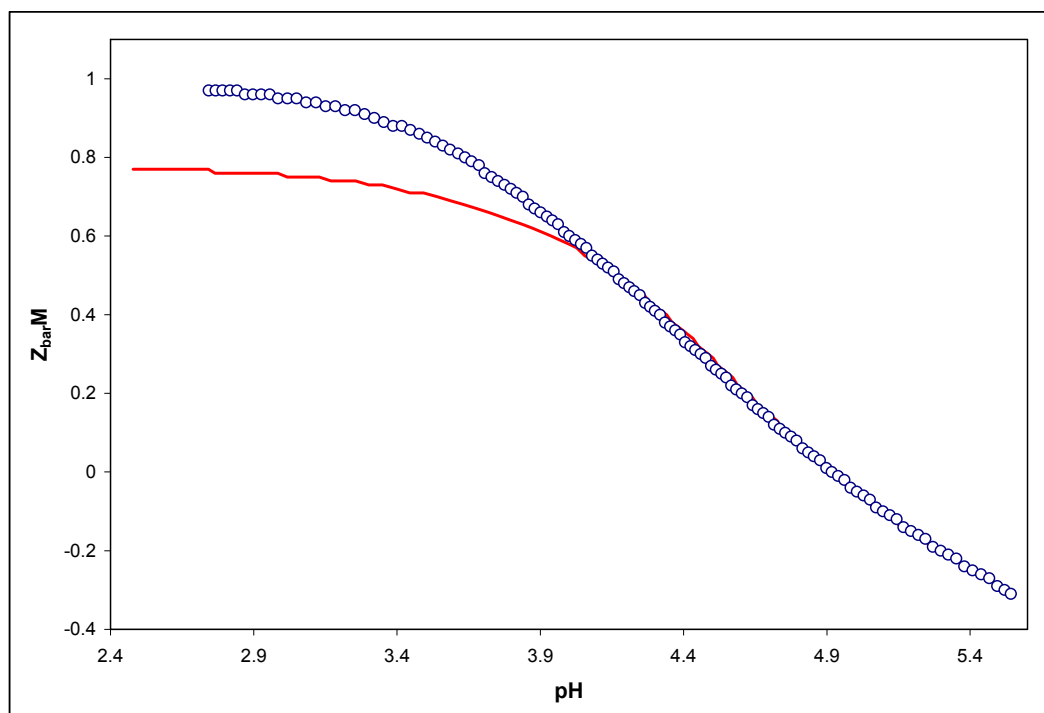


Figure 4.6: Experimental (circle) and theoretical (solid line) potentiometric protonation curve in the pH range between 2.3 and 5.8 for Cr^{III} -Bpy system studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T:M_T$ ratio 4, $L_T = 8.2 \times 10^{-3}\text{M}$, $M_T = 1.8 \times 10^{-3}\text{M}$. The model was ML and $\text{ML}(\text{OH})_3$ in the presence of all chromium hydroxo species.

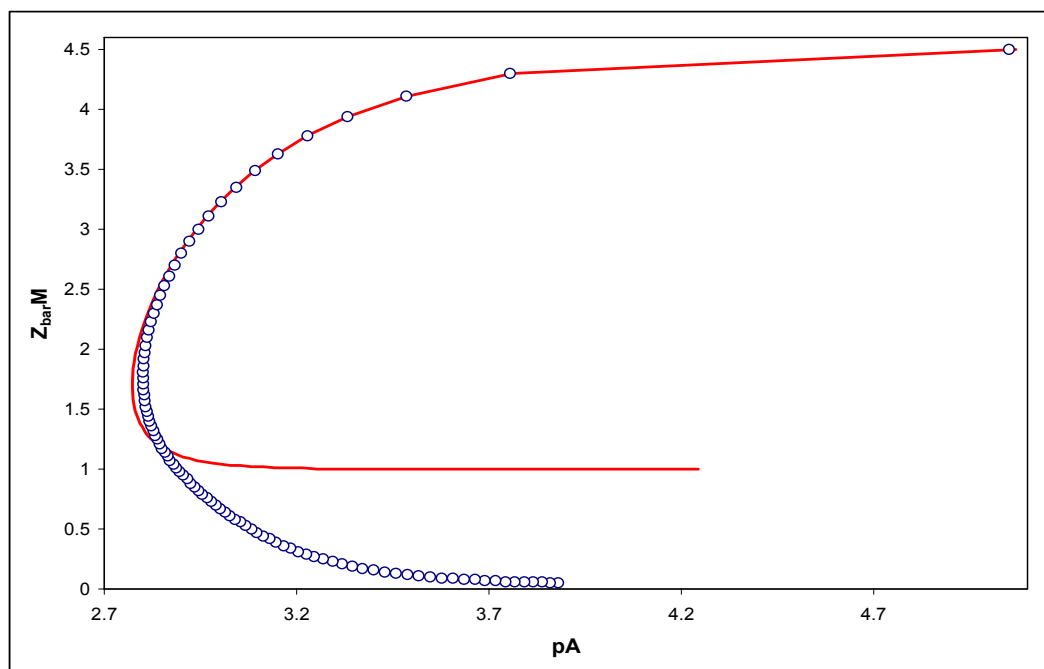


Figure 4.7: Experimental (circle) and calculated (solid line) complex formation curve for Cr^{III} -Bpy system studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T:M_T$ ratio 4, $L_T = 8.2 \times 10^{-3}\text{M}$; $M_T = 1.8 \times 10^{-3}\text{M}$. The model was ML and $\text{ML}(\text{OH})_3$ in the presence of all chromium hydroxo species.

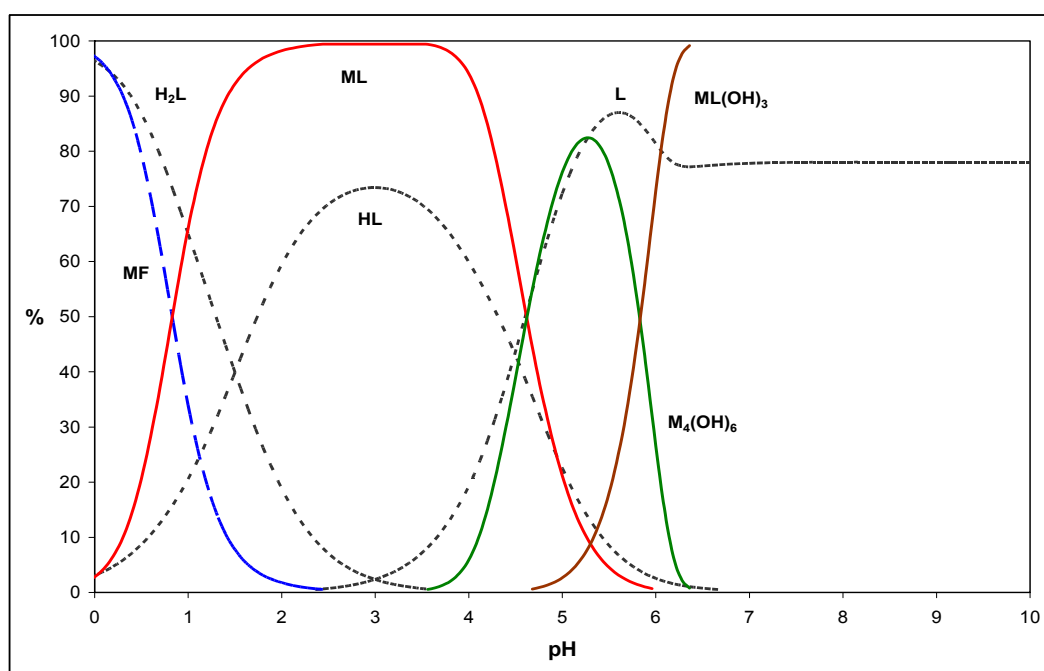


Figure 4.8: The species distribution as a function of pH calculated for Cr^{III} -Bpy system (in presence of chromium hydroxo polynuclear species) based on potentiometric results reported in this work at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T = 8.2 \times 10^{-3}\text{M}$; $M_T = 1.8 \times 10^{-3}\text{M}$; $L_T:M_T = 4$. Solid lines represent fractions of the total chromium concentration M_T for chromium complexes with the ligand Bpy. Dotted lines represent fractions of the total ligand concentration L_T in solution.

Refinement according the second assumption

It has been reported that all chromium metal hydroxo polynuclear species had an exceedingly slow kinetics and all chromium metal hydroxo mononuclear species were kinetically fast [117]. Rai et al [39] reported that only CrOH is the predominant species in solution between pH 2.6 and 6.5. The formation of chromium mononuclear species [CrOH and Cr(OH)₂] was checked during the refinement operation using ESTA program. The test consisted of a refinement procedure allowing these mononuclear chromium metal hydroxo species to compete with other complexes. Only CrOH was refined by ESTA, Cr(OH)₂ was rejected. That test confirmed what was reported by Rai et al.

From that test and on the basis of the bad fits obtained in assumption one, in the second assumption all chromium metal hydroxo polynuclear species [Cr_x(OH)_y] and Cr(OH)₂ were excluded from the refinement operation. Only CrOH was included in the model.

During the refinement operations, many attempts were used to refine the model proposed in Table 4.4. All refinement operations started with a simplest model. ML; ML and MLOH; ML, MLOH and ML(OH)₂; ML, MLOH,

ML(OH)₂ and ML(OH)₃; ML, MLOH, ML(OH)₂, ML(OH)₃ and ML₂; finally ML, MLOH, ML(OH)₂, ML(OH)₃ and ML₃. The model including ML, MLOH, ML(OH)₂ and ML(OH)₃ was refined by ESTA program. All potentiometric data were treated as it comes from potentiometric experiment, nothing was refined. The fits resulted in high standard deviations and Hamilton R-factor.

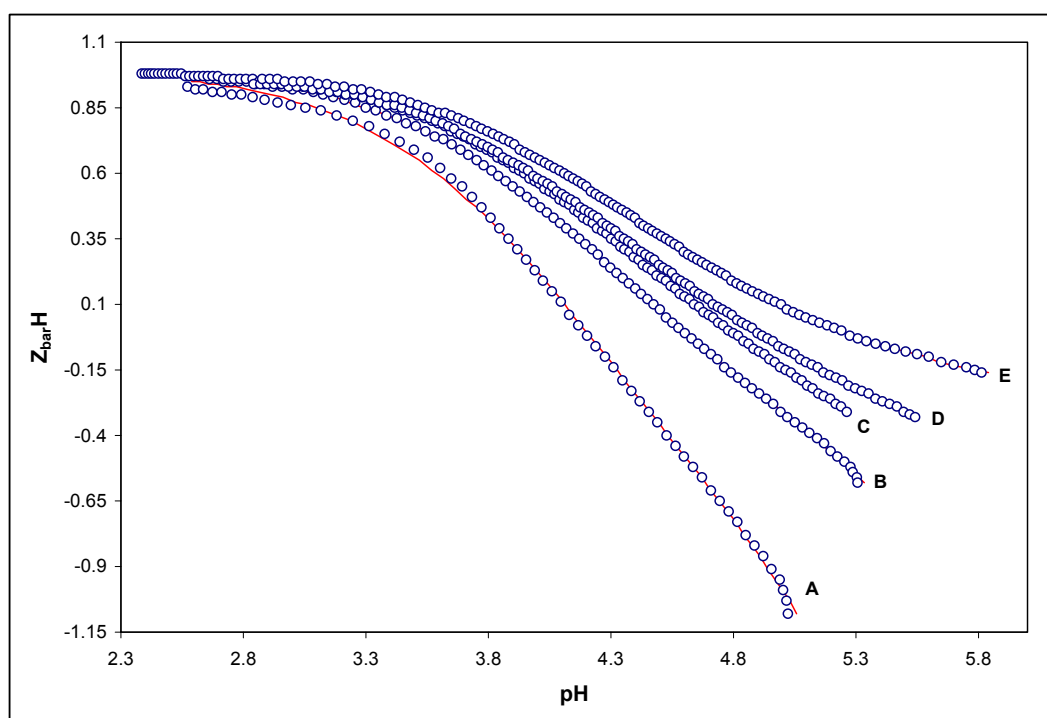


Figure 4.9: Experimental (circle) and calculated (solid line) potentiometric protonation curve for Cr^{III}-Bpy system studied by GEP at 25°C and ionic strength 0.1 M in NaNO₃ for different L_T:M_T ratios (A = ratio 1, B = ratio 2, C = ratio 3, D = ratio 4 and E = ratio 9). The model ML, MLOH, ML(OH)₂ and ML(OH)₃ were refined in the presence of CrOH.

The analysis of the standard deviations, the Hamilton R-factor, and the behavior of the experimental potentiometric formation $\bar{Z}_H$ and $\bar{Z}_M$ curves were an indication of how to proceed in order to improve the fit.

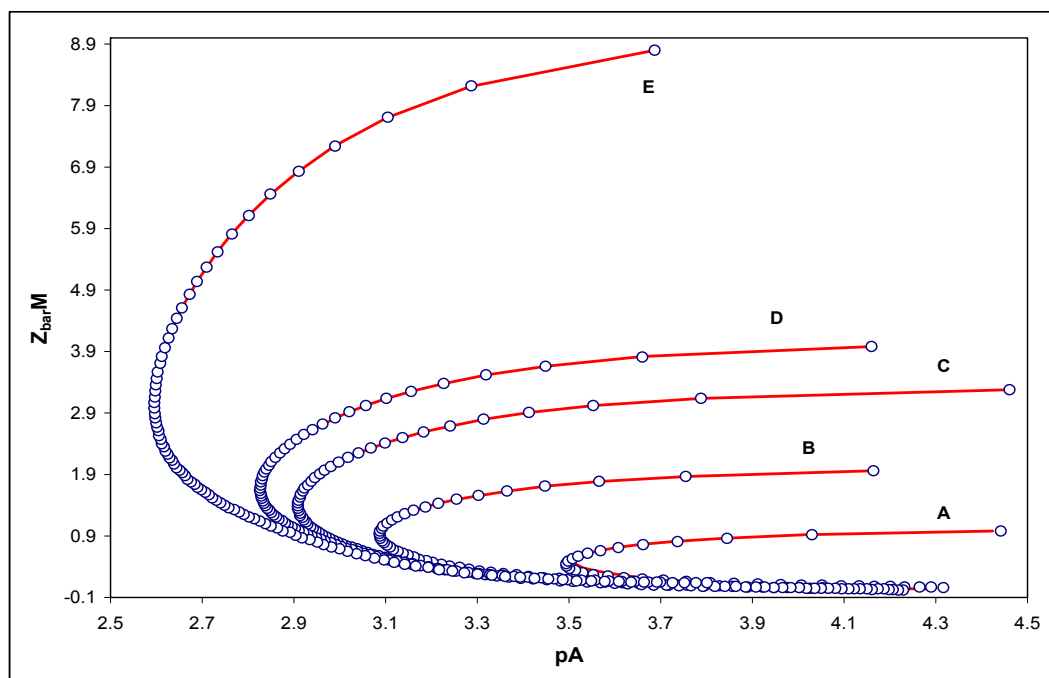


Figure 4.10: Experimental (circle) and calculated (solid line) complex formation curve for Cr^{III} -Bpy system studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 for different $L_T:M_T$ ratios (A = ratio 1, B = ratio 2, C = ratio 3, D = ratio 4 and E = ratio 9). The model ML , MLOH , $\text{ML}(\text{OH})_2$ and $\text{ML}(\text{OH})_3$ were refined in the presence of CrOH .

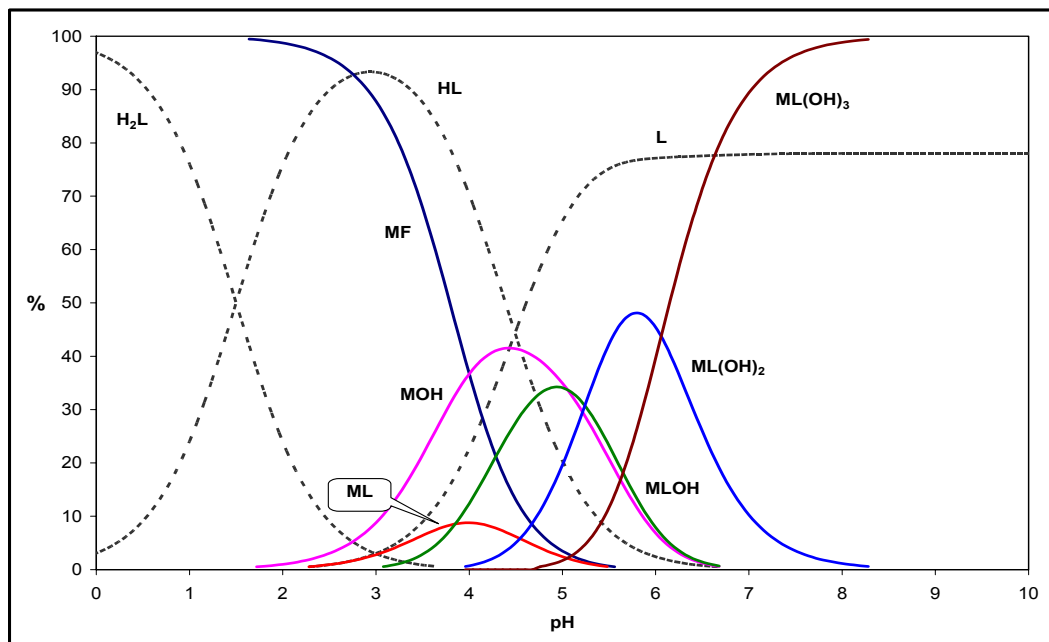


Figure 4.11: The species distribution as a function of pH calculated for Cr^{III} -Bpy system based on potentiometric results reported in this work at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T = 8.2 \times 10^{-3}$ M; $M_T = 1.8 \times 10^{-3}$ M; $L_T:M_T = 4$. Solid lines represent fractions of the total chromium concentration M_T for chromium complexes with the ligand Bpy. Dotted lines represent fractions of the total ligand concentration L_T in solution.

The first step consisted of deletion of data points affected by precipitation (data points between ellipses - see Figures 4.4-4.5). The second step involved the refinement of the acid concentration. Any attempt to refine the base concentration resulted in a correlation between some complexes. ESTA did not like to refine the metal ions concentration and the refinement of the ligand concentration did not change the stability constants and the relative standard deviations.

An alternative approach considered the refinement of ML_2 and ML_3 species. For $L_T:M_T$ ratio 2, ESTA could not refine ML_2 in the presence of ML. ML_2 was refined only when ML was excluded from the model. Even for $L_T:M_T$ ratio 3, ESTA did not refined ML_2 in the presence of ML, the refinement of ML_3 resulted in a correlation between all complexes. For $L_T:M_T$ ratio 4, ESTA refined ML_2 in the presence of ML. The refinement of ML_3 in the presence of ML resulted in correlation between $ML(OH)$ and $ML(OH)_3$. For $L_T:M_T$ 9 both ML_2 and ML_3 were not refined in the presence of ML. ML_3 was totally rejected but ML_2 was refined when ML was excluded from the model.

The overall metal-ligand model: ML, MLOH, ML(OH)₂, and ML(OH)₃ resulted in an excellent optimisation with ESTA software package (Table 4.4). The calculated and experimental potentiometric formation $\bar{Z}_H$ and $\bar{Z}_M$ curves appear in Figures 4.9-4.10. The species distribution diagram plotted as a function of pH for that case shows (in the absence Cr_x(OH)_y species and Cr(OH)₂) the competition between CrOH, ML, MLOH, ML(OH)₂, and ML(OH)₃ from pH 2 to pH 9 - see Figure 4.11.

Table 4.4: Formation constants for chromium with Bpy found in this work at 25°C and ionic strength 0.1 M in NaNO₃ by glass electrode potentiometry (GEP), L_T:M_T ratio 1, 2, 3, 4, 9 and overall. Data refined in the presence of CrOH.

Species	Ratio 1 Log β	Ratio 2 Log β	Ratio 3 Log β	Ratio 4 Log β	Ratio 9 Log β	Overall (ratios 3+4) Log β
ML	–	1.35 ± 0.071	1.25 ± 0.081	2.11 ± 0.033	1.98 ± 0.037	2.14 ± 0.025
ML₂	–	–	–	4.57 ± 0.086	–	–
MLOH	11.60 ± 0.056	11.59 ± 0.011	11.97 ± 0.005	12.04 ± 0.015	12.49 ± 0.004	12.02 ± 0.009
ML(OH)₂	20.37 ± 0.107	19.84 ± 0.040	20.36 ± 0.016	20.58 ± 0.012	20.77 ± 0.007	20.64 ± 0.011
ML(OH)₃	29.23 ± 0.055	28.66 ± 0.011	28.81 ± 0.012	28.30 ± 0.026	28.19 ± 0.012	28.25 ± 0.034
Hamilton R-factor	0.0053	0.0016	0.0011	0.0021	0.0026	0.0039

Refinement according the third assumption

Even though a good fit was obtain for $L_T:M_T$ ratio 2, 3, 4 and 9 (Figures 4.9-4.10), the complex formation curve for $L_T:M_T$ ratio 1 (Figure 4.12) was still not good enough compared with the fits obtained for higher ratios. The model refined for $L_T:M_T$ ratio 1 can be seen in Table 4.4. Figure 4.12 illustrate the behavior of the complex formation curve for $L_T:M_T$ ratio 1. It can be seen in Figure 4.12 that the fits of the $\bar{Z}_M$ function is not good. From that observation and what had been reported by Rai et al [39], it can be assumed that $CrOH$ species was not formed during the experimental time scale. It has also been reported that [118]: in aqueous solutions chromium complexes are characterized by their relative kinetic inertness. "Ligand displacement reactions of Cr^{III} complexes are only 10 times faster than those of Co^{III} , with half times in the range of several hours. It is largely because of this kinetic inertness that so many complex species can be isolated as solids and that they persist for relatively long periods of time in solution, even

under conditions of marked thermodynamic instability” [118].

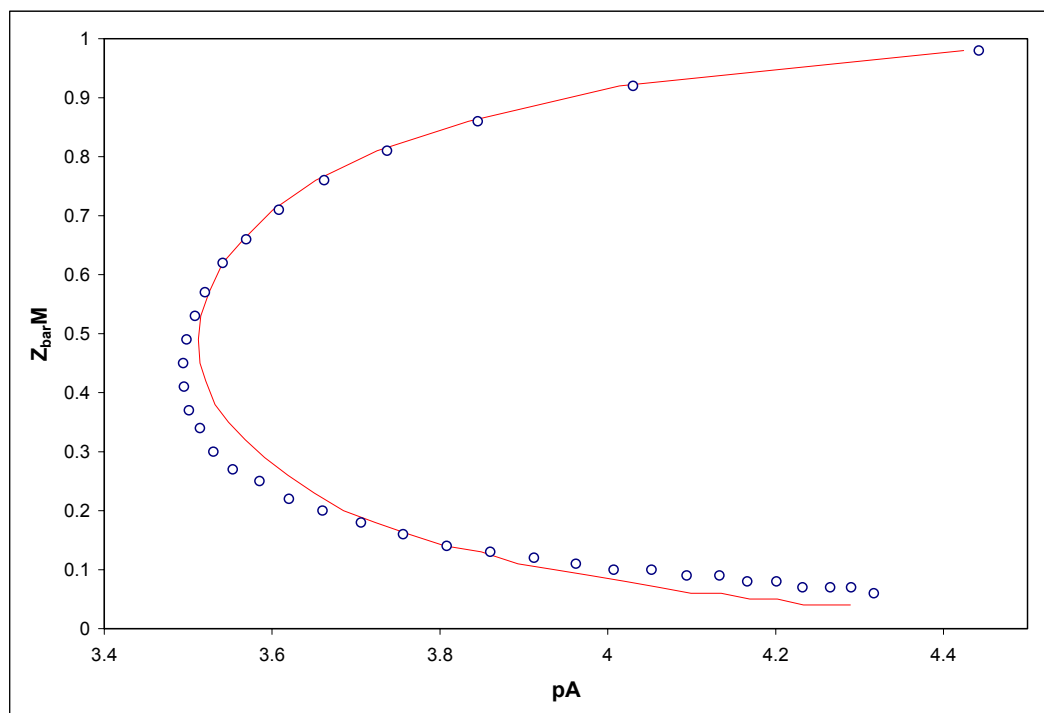


Figure 4.12: Experimental (circle) and calculated (solid line) complex formation curve for Cr^{III} -Bpy system studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T:M_T$ ratio 1 $L_T = 5.1 \times 10^{-3}\text{M}$; $M_T = 4.9 \times 10^{-3}\text{M}$. MLOH , $\text{ML}(\text{OH})_2$ and $\text{ML}(\text{OH})_3$ were refined in the presence of CrOH .

In the refinement operation according to the third assumption, CrOH species was also excluded from the refinement operation. The fits obtained from that operation resulted in the lowest standard deviations and Hamilton R-factor for both calculated and experimental potentiometric formation $\bar{Z}_H$ and $\bar{Z}_M$ curves. Table 4.5 reports the suggested model and the refined values of stability constants for $L_T:M_T$ ratio 1 in the absence of CrOH .

During the refinement operation according to the third assumption, for $L_T:M_T$ ratio 1, ML was refined. For $L_T:M_T$ ratio 2, ML_2 was refined. For $L_T:M_T$ ratio 3, ML_3 was not refined. For $L_T:M_T$ ratio 4 and 9, ML_3 was not refined even if we had large excess of ligand. The fit for the complex formation curve obtained for $L_T:M_T$ ratio 1, is by far better than the one obtained according to assumption one. Figure 4.13 illustrates the behavior of the complex formation curve for $L_T:M_T$ ratio 1.

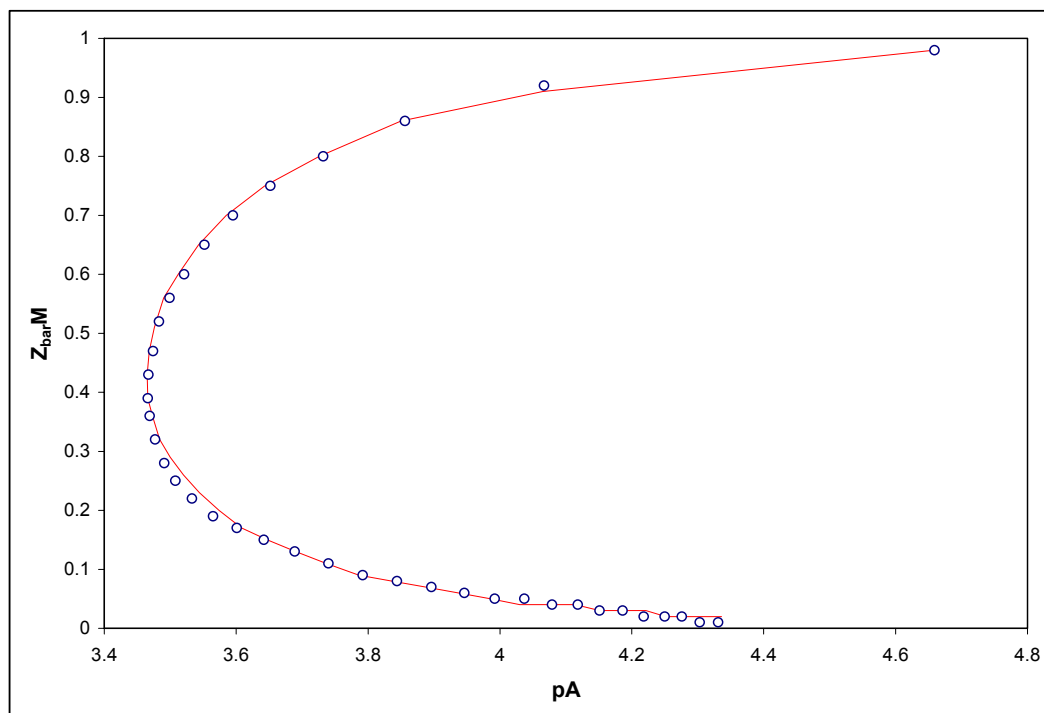


Figure 4.13: Experimental (circle) and calculated (solid line) complex formation curve for Cr^{III} -Byp system studied by GEP at 25°C and ionic strength 0.1 M in $NaNO_3$. $L_T:M_T$ ratio 1 $L_T= 5.1 \times 10^{-3}M$; $M_T= 4.9 \times 10^{-3}M$. ML, MLOH, $ML(OH)_2$ and $ML(OH)_3$ were refined. CrOH was excluded from the refinement operation.

Table 4.5: Formation constants for chromium with Bpy found in this work at 25°C and ionic strength 0.1 M by glass electrode potentiometry (GEP), $L_T:M_T$ ratio 1, 2, 3, 4 and 9. Data refined excluding all $Cr_x(OH)_y$ species.

Species	Ratio 1 Log β	Ratio 2 Log β		Ratio 3 Log β		Ratio 4 Log β		Ratio 9 Log β	
		Model I	Model II	Model I	Model II	Model I	Model II	Model I	Model II
ML	2.55 (± 0.008)	2.79 (± 0.003)	2.73 (± 0.004)	2.82 (± 0.003)	2.79 (± 0.006)	2.58 (± 0.011)	2.36 (± 0.023)	2.52 (± 0.013)	2.17 (± 0.020)
ML₂	–	–	4.99 (± 0.023)	–	4.75 (± 0.056)	–	5.10 (± 0.030)	–	5.11 (± 0.014)
MLOH	12.62 (± 0.003)	12.36 (± 0.002)	12.31 (± 0.003)	12.38 (± 0.002)	12.34 (± 0.005)	12.27 (± 0.006)	11.56 (± 0.009)	12.44 (± 0.005)	12.32 (± 0.005)
ML(OH)₂	20.44 (± 0.058)	19.87 (± 0.044)	20.22 (± 0.016)	20.34 (± 0.013)	20.43 (± 0.014)	19.84 (± 0.052)	20.16 (± 0.022)	20.37 (± 0.014)	20.45 (± 0.005)
ML(OH)₃	29.47 (± 0.020)	28.64 (± 0.015)	28.45 (± 0.017)	28.62 (± 0.011)	28.53 (± 0.016)	28.36 (± 0.017)	28.17 (± 0.023)	27.89 (± 0.025)	27.52 (± 0.027)
Hamilton R-factor	0.0017	0.0016	0.0009	0.0018	0.0016	0.0044	0.0032	0.0026	0.0011

Final model of Cr^{III}-Bpy system

The refinement operations mentioned in the three assumptions showed how difficult it was to establish the model of the Cr^{III}-Bpy system. In order to decide on the final model for that system, all potentiometric protonation curves $\bar{Z}_H$ were plotted together - see Figure 4.14. The reason for that was the verification of where the precipitation started to occur for each titration, to see the general trend of all titrations and finally to decide which ratios would be used for a combined refinement to generate the final model.

A deviation was observed on the $\bar{Z}_H$ function at around pH 5 for L_T:M_T ratios 1 and 2. That deviation was an indication of the beginning of the precipitation, even if it was only visible at around pH 5.8. According to Figure 4.14, L_T:M_T ratio 1 did not follow the pattern followed by other ratio. For L_T:M_T ratio 2, it is clear that the experiment did not start well. Ratios 3, 4, and 9 were less disturbed when compared with L_T:M_T ratios 1 and 2. This can be explained by the excess of the ligand concentration and the postponement of the precipitation to high pH values.

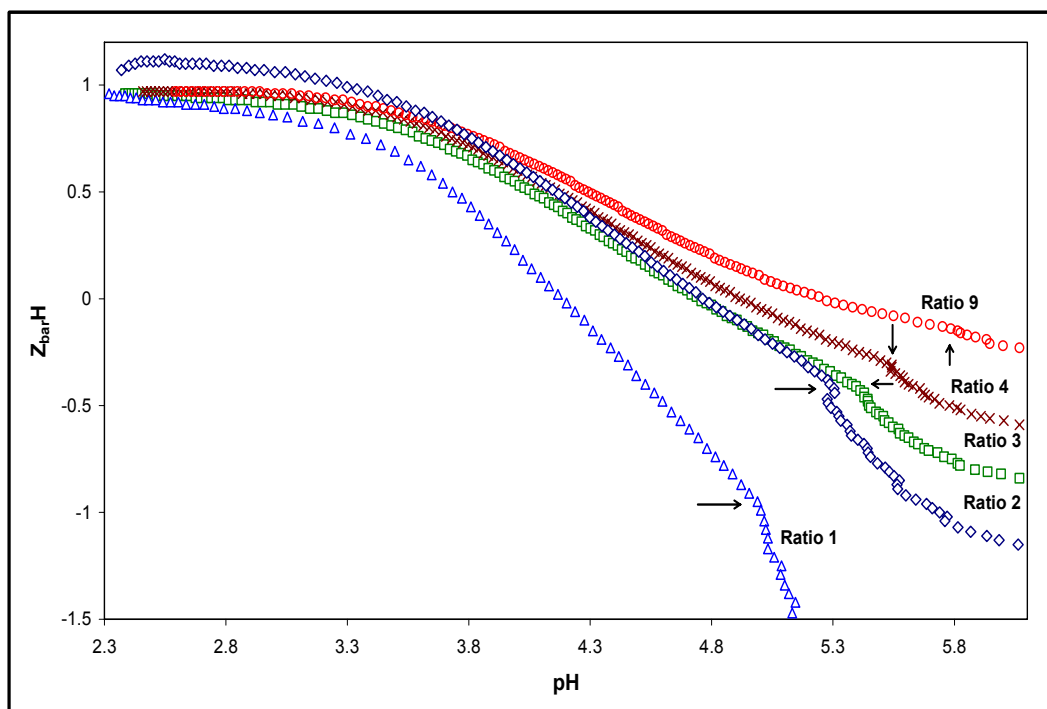
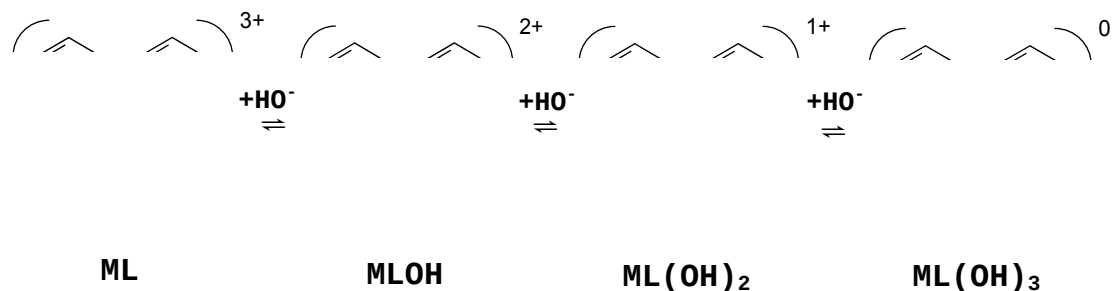


Figure 4.14: Experimental protonation formation curve for Cr^{III} -Byp system studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T:M_T$ ratio 1 (triangle), $L_T:M_T$ ratio 2 (diamond), $L_T:M_T$ ratio 3 (square), $L_T:M_T$ ratio 4 (multiplication sign), and $L_T:M_T$ ratio 9 (circle). Arrows indicate where the precipitation is suspected to start.

$L_T:M_T$ ratios 3 and 4 were selected for the refinement of the overall stability constants. $L_T:M_T$ ratio 9 uses a large excess of ligand concentration when compared to that of the metal ion and might be seen as a pK_a determination. The analysis of $\bar{Z}_M$ (Figure 4.15) curves did not show any evidence of the presence of ML_2 complex. It shows a strong evidence of the predominance of hydrolyzed complexes. The analysis of data in Table 4.5 also showed that when ML_2 is included in the model, increases in the standard deviations of all other suggested complexes arise. From these observations it

is clear that the reaction is mainly due to the formation of ML followed by its hydrolysis. The reaction below represents the equilibrium involved in that particular case.



Because of the relative kinetic inertness of chromium complexes, the reaction from ML to ML₂ is very slow. ML₂ is not present in any significant concentration making the current determination of its stability constant not accurate. ML₃ complex could not be refined in the presence of ML₂ simply because ML₃ takes longer time to be formed than ML₂ and our experimental time scale did not allow this complex to be formed. During the refinement operation, only the acid concentration was refined. The variation of the concentration is shown in the following table.

Table 4.6: Refinement of acid concentration for potentiometric experiments of Cr^{III}-Bpy system.

Ratio	[H ⁺] Before	[H ⁺] After	% change
1	0.01150	0.0115258	+ 0.22
2	0.01150	0.0105507	- 8.25
3	0.01150	0.0116759	+ 1.53
4	0.01142	0.0112554	- 1.44
9	0.01146	0.0113638	- 0.84

The refinement operation performed in the presence or the absence of CrOH species did not change the speciation model. The stability constant for the ML complex is however affected. All chromium hydroxo species $ML(OH)_x$ stayed more or less at the same values (Table 4.5). Table 4.7 gives the stability constant values refined for Cr^{III} -Bpy complexes for the final model. The model includes ML, ML_2 , MLOH, $ML(OH)_2$ and $ML(OH)_3$ species. In Figures 4.15 is plotted the $\bar{Z}_M$ function versus pA and in Figure 4.16 is plotted the species distribution diagram as a function of pH for the combined refinement. This diagram will be helpful in the interpretation of voltammetric results in the next section.

Table 4.7: Overall stability constants for chromium with Bpy found in this work at 25°C and ionic strength 0.1 M in $NaNO_3$ by glass electrode potentiometry (GEP). Data refined without CrOH.

Species	Final model Log β
ML	2.63 ± 0.014
ML_2	5.09 ± 0.044
MLOH	12.26 ± 0.011
$ML(OH)_2$	20.55 ± 0.019
$ML(OH)_3$	28.35 ± 0.037
Hamilton R-factor	0.0039

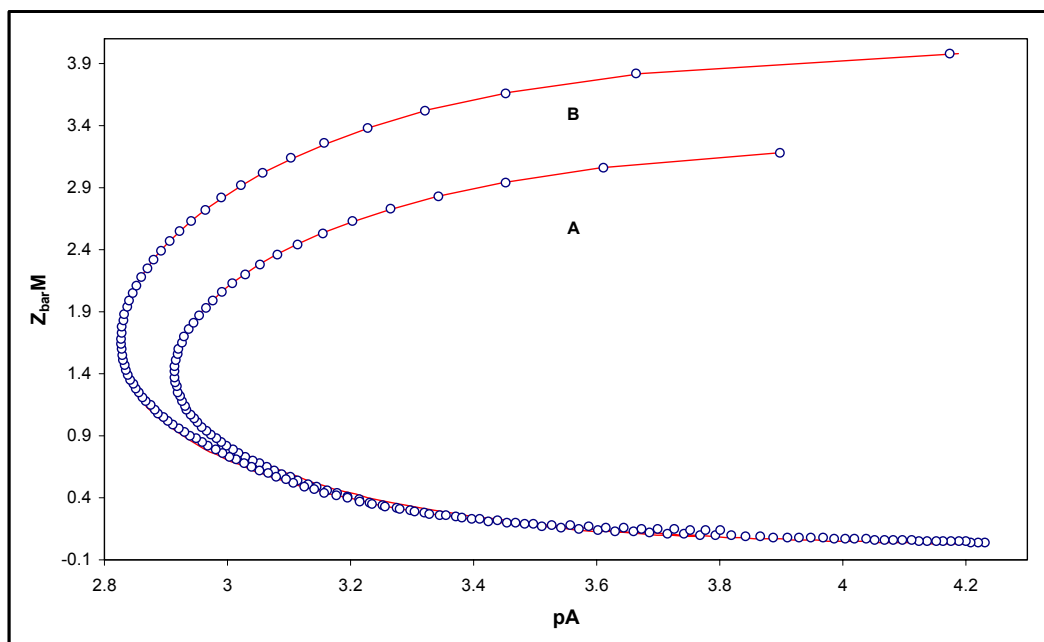


Figure 4.15: Experimental (circle) and calculated (solid line) overall complex formation curve for Cr^{III} -Bpy system studied by GEP at 25°C and ionic strength 0.1 M in NaNO_3 . The model ML , ML_2 , MLOH , $\text{ML}(\text{OH})_2$ and $\text{ML}(\text{OH})_3$ were refined in the absence of CrOH (A: $L_T:M_T$ = ratio 3, B: $L_T:M_T$ = ratio 4).

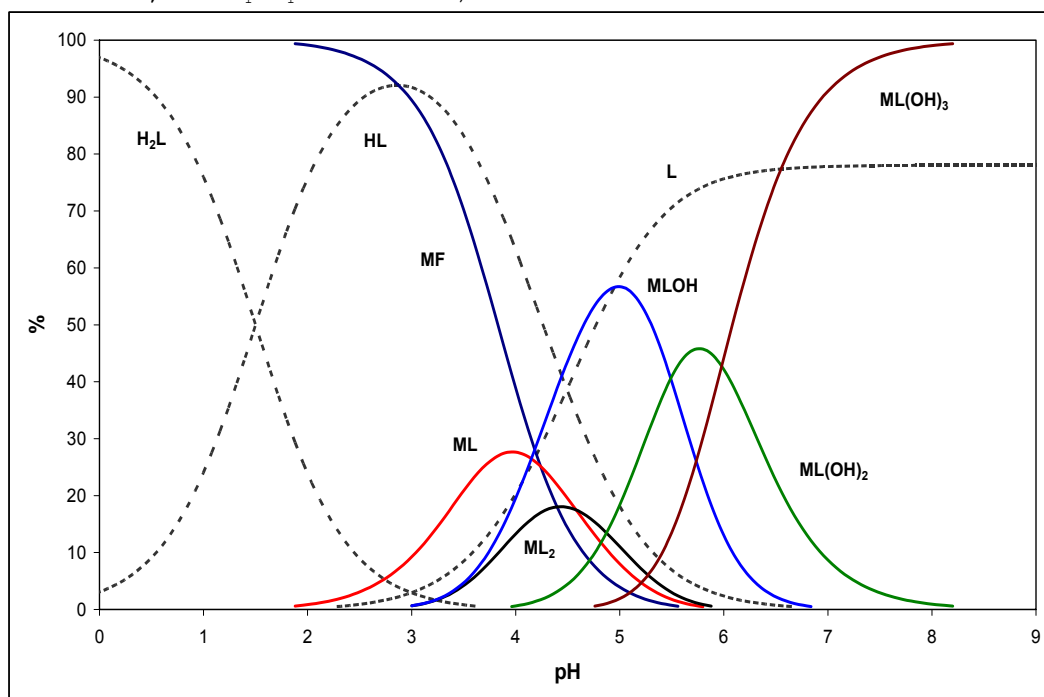


Figure 4.16: The species distribution as a function of pH calculated for the overall model for Cr^{III} -Bpy system based on potentiometric results reported in this work at 25°C and ionic strength 0.1 M in NaNO_3 . $L_T = 8.2 \times 10^{-3}$ M; $M_T = 1.8 \times 10^{-3}$ M; $L_T:M_T = 4$. Solid lines represent fractions of the total chromium concentration M_T for chromium complexes with the ligand Bpy. Dotted lines represent fractions of the total ligand concentration L_T in solution. Species distribution plotted for the model in Table 4.7.

4.2. Voltammetry

4.2.1. AC studies of Bpy

The adsorption phenomenon has been investigated by use of alternating current voltammetry. The behavior of the background electrolyte alone is different from the one containing the ligand and finally from the same background electrolyte containing the ligand and metal ion together. In the presence of an adsorption of a compound onto the HMDE we observe an ACV adsorption and a desorption peak. If there is no adsorption or desorption peak recorded, a change in the capacitance of the double layer, which also confirms an adsorption phenomenon, can be seen.

Figures 4.17-4.18 show the adsorption of Bpy in a neutral electrolyte (NaNO_3) at pH 5.8 containing no buffer. The adsorption can be seen in the lowering of the capacitance of the double layer. The adsorption is more pronounced as the ligand concentration is increased. At around -1.3 V Bpy is reduced. After that reduction the ligand showed an increase in the adsorption by the lowering of the recorded AC current see Figure 4.17.

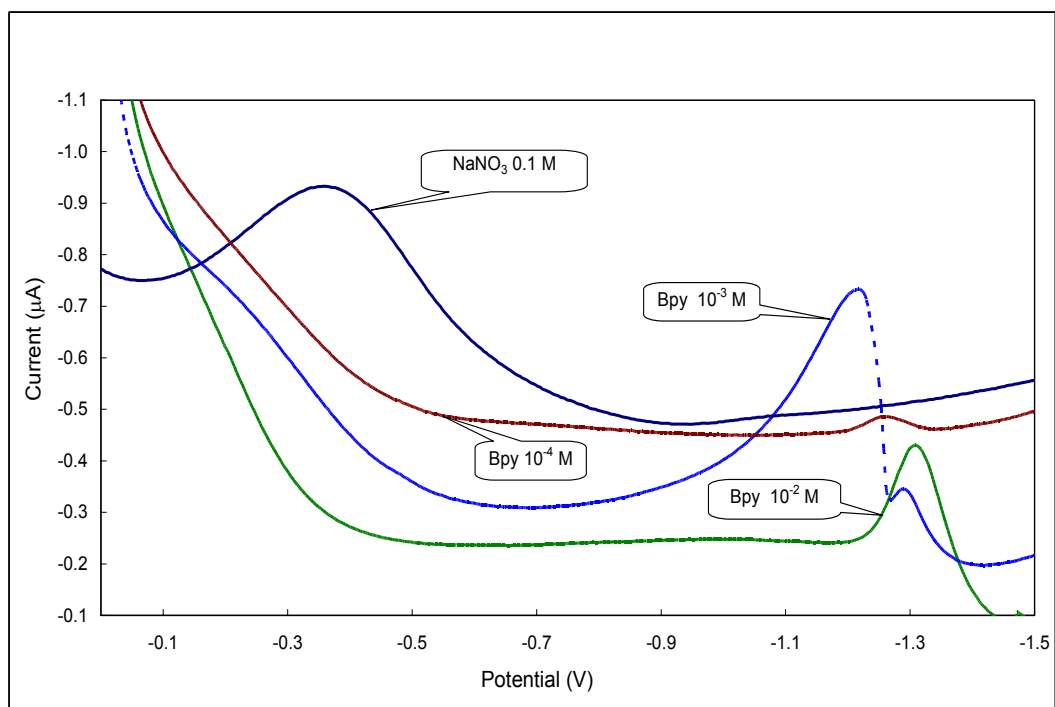


Figure 4.17: AC voltammograms of Bpy at different concentrations in 0.1 M sodium nitrate adjusted to pH 5.8. t_d : 0 s, HMDE used as working electrode.

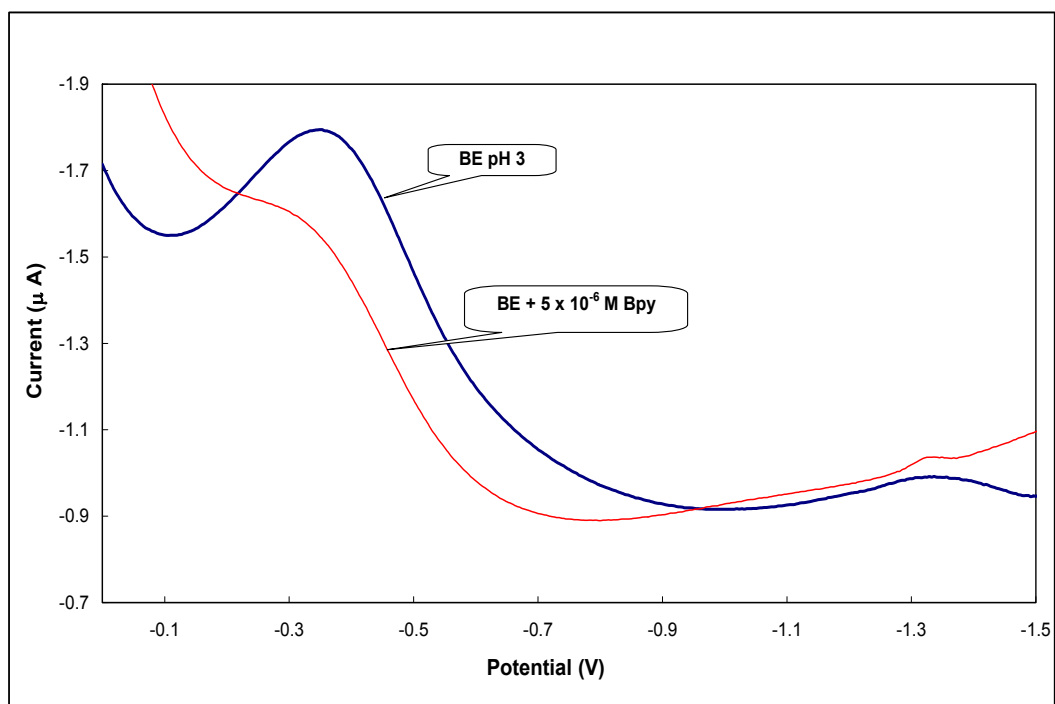


Figure 4.18: AC voltammograms of 5×10^{-6} M Bpy in 0.1 M sodium nitrate adjusted to pH 5.8. t_d : 30 s, HMDE used as working electrode.

Influence of pH

The pH plays a very important role in solution chemistry. Bpy can be present in a solution in three different forms. Depending on a pH of a solution, two protonated forms (H_2L and HL) and the deprotonated form (L) are shown in Figure 4.3. At each pH value, there will be a certain percentage of each species in the solution. The AC voltammograms can be interpreted by comparing the information provided with the one given by the species distribution plotted as a function of pH.

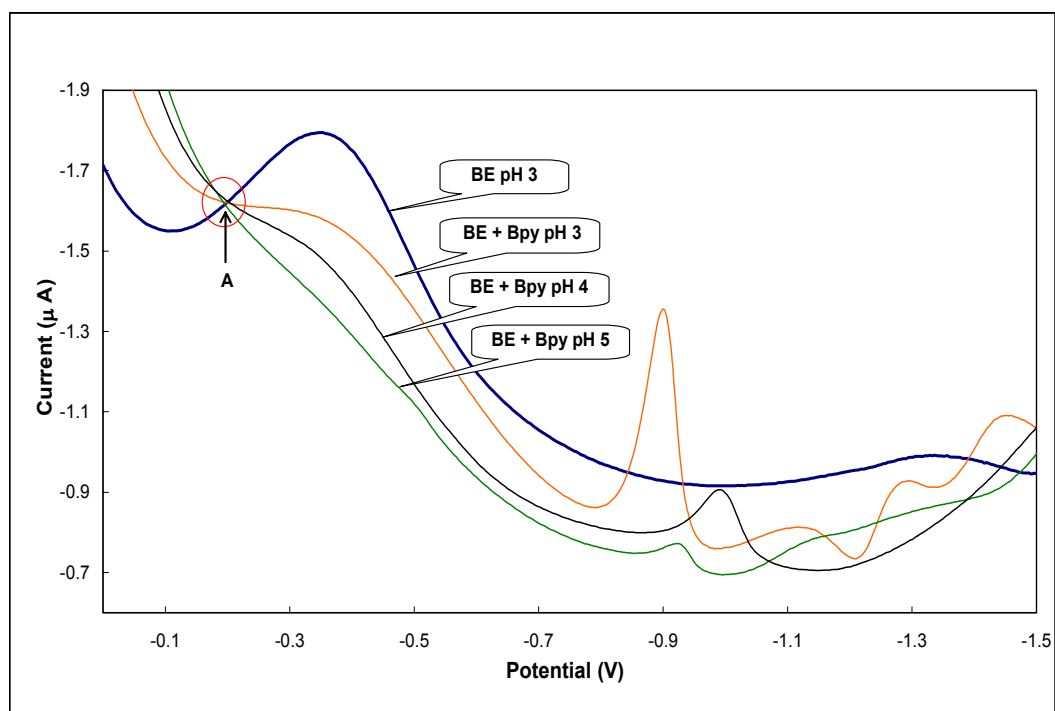


Figure 4.19: AC voltammograms of 5×10^{-6} M Bpy in 0.1 M (H, Na)NO₃ recorded at different pH values between 3 and 5, t_d : 30 s.

Figure 4.19 shows the ACV behavior of Bpy between pH 3 to 5. According to the species distribution diagram

plotted as a function of pH (Figure 4.3) in that pH range the HL form of the ligand is the dominant ligand species. By increasing the pH from 3 to 5, a lowering of the capacitance of the double layer is observed in Figure 4.19. The peak at -0.9 V recorded at pH 3 decreases considerably and at pH 5 according the species distribution diagram, we have in solution a mixture of the HL and L forms of the ligand with predominance of the deprotonated form (L). It is quite clear from Figure 4.19 that the adsorption of Bpy is pH dependent and it also depends on the form of the ligand present in a solution. The deprotonated form (L) of the ligand is strongly adsorbed at potentials more positive than -0.9 V as seen in Figure 4.20. The protonated form (HL) is also adsorbed from -0.2 V to approximately -1.5 V - see Figure 4.19.

In Figures 4.19, an interesting behavior showed by a circle A was observed on these voltammograms. This behaviour is called isosbestic point on UV-visible spectrum, and is recorded for a number of solutions containing for instance, a constant amount of the metal but with the increasing ligand concentrations.

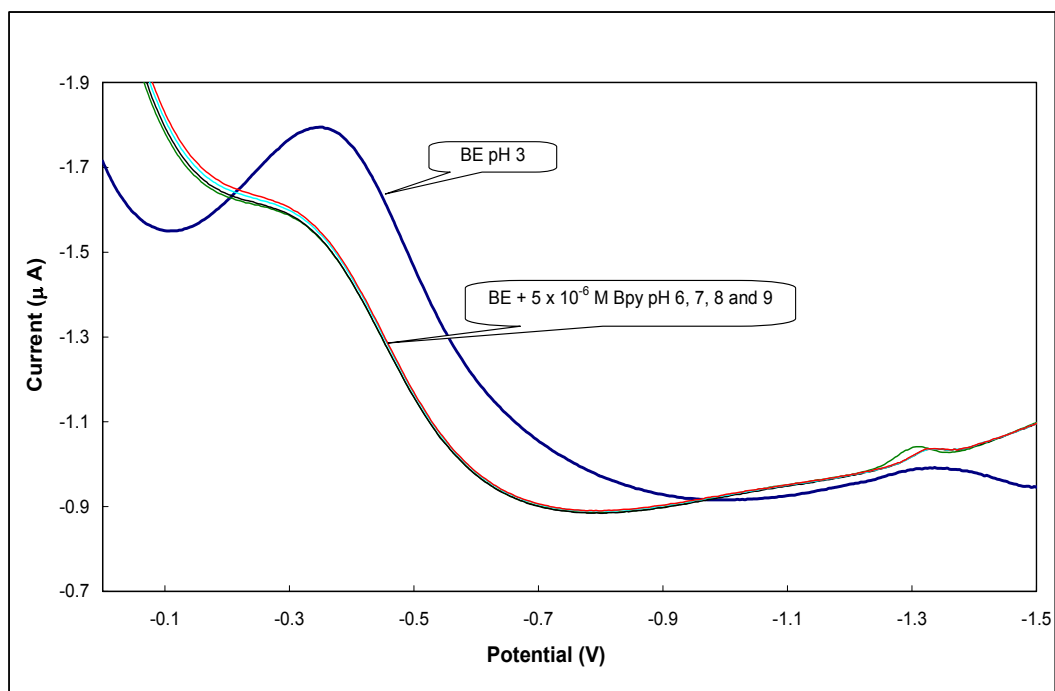


Figure 4.20: AC voltammograms of 5×10^{-6} M Bpy in 0.1 M (H, Na)NO₃, recorded at different pH values.

All spectra are superimposed and the presence of a spectrally invariant point produced by intersection is noted. The presence of such a point indicates the presence of two independent species, which differ in their ligand to metal ratio being at equilibrium. Hence it must be supplemented by other methods to define reliably the number and the kind of species present [103]. According to Figure 4.19, the isosbestic point A shows in that case the presence in the solution of two different forms of the ligand (HL and L).

Ammonium buffer (NH₄Cl/NH₄OH pH 9.3) was reported as supporting electrolyte in the determination of Cr^{III}

using Bpy [84-87]. Figure 4.21 shows AC voltammograms recorded for sodium nitrate and ammonium buffer. A large decrease in AC current is observed in Figure 4.21 for ammonium buffer when compared with sodium nitrate.

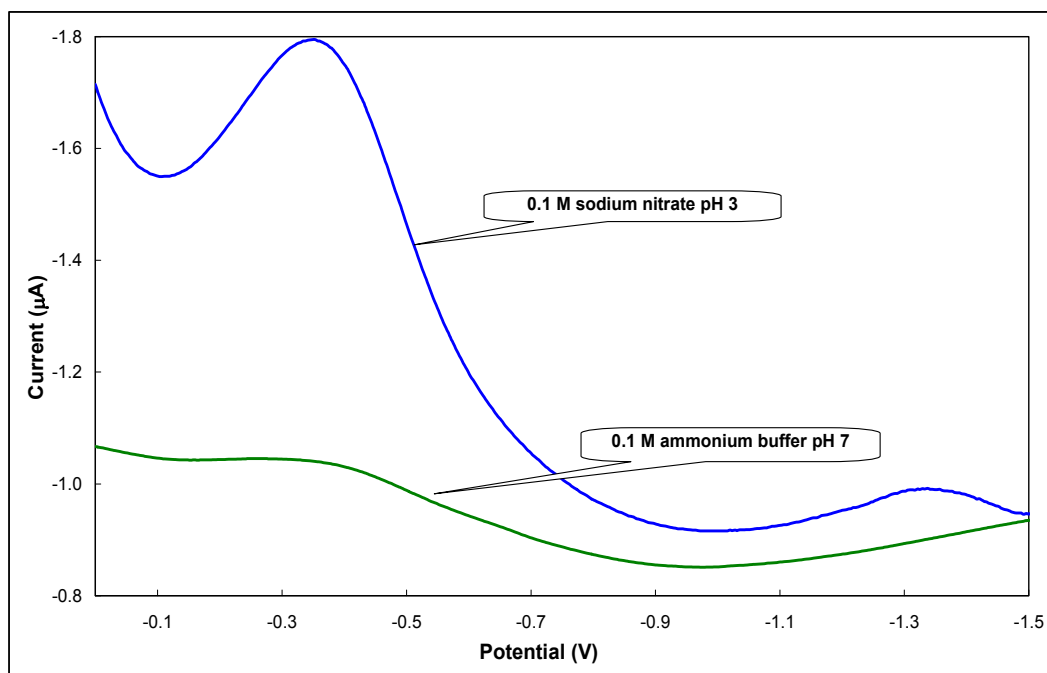


Figure 4.21: AC voltammograms of 0.1 M (H, Na)NO₃ compare with 0.1 M NH₄Cl/NH₄OH.

In sodium nitrate the adsorption of Bpy was pH dependent. Between pH 6 and 9 no change in recorded AC voltammograms was observed - see Figure 4.20. This was explained by the presence of only one form of the ligand (L) in the solution. The AC behavior of Bpy in ammonium buffer is shown in Figures 4.21-4.22. In Figure 4.22, from pH 7 to 9, Bpy showed a decrease in adsorption; the recorded AC voltammograms were recorded closer to the background electrolyte voltammogram. The reduction peak of Bpy shifted to more negative

potentials from position A to B and finally to C between pH 7 and 9. This shift could be attributed to the activity of Bpy at the HMDE. This shifting with pH suggests involvement of protons in the electrochemical reaction. Figure 4.24 shows clearly that the peak recorded by AC voltammetry (Figure 4.22) was related to the reduction of Bpy and not to a desorption peak. In Figure 4.23 from pH 9 to 9.5 a large decrease in the recorded AC current is observed in the potential range between -500 mV and -900 mV. From that observation, a deposition potential (E_d) in that potential range should be suitable for the accumulation of Bpy (-1 V is commonly used [84-87]). No change in the recorded AC voltammograms was observed for L form of Bpy when the pH was increased from 6 to 9 -see Figure 4.20. In Figure 4.23, where ammonium buffer was used as supporting electrolyte, a large decrease in the recorded AC current was observed as the pH was increased. By comparing Figures 4.20 and 4.23, the only difference is the composition of the supporting electrolyte. The change in recorded AC current in ammonium buffer from pH 9 to 9.5 could not be related to the L form of Bpy but to the couple $\text{NH}_3/\text{NH}_4^+$ or some interaction between Bpy and NH_4^+ ions at the electrode surface.

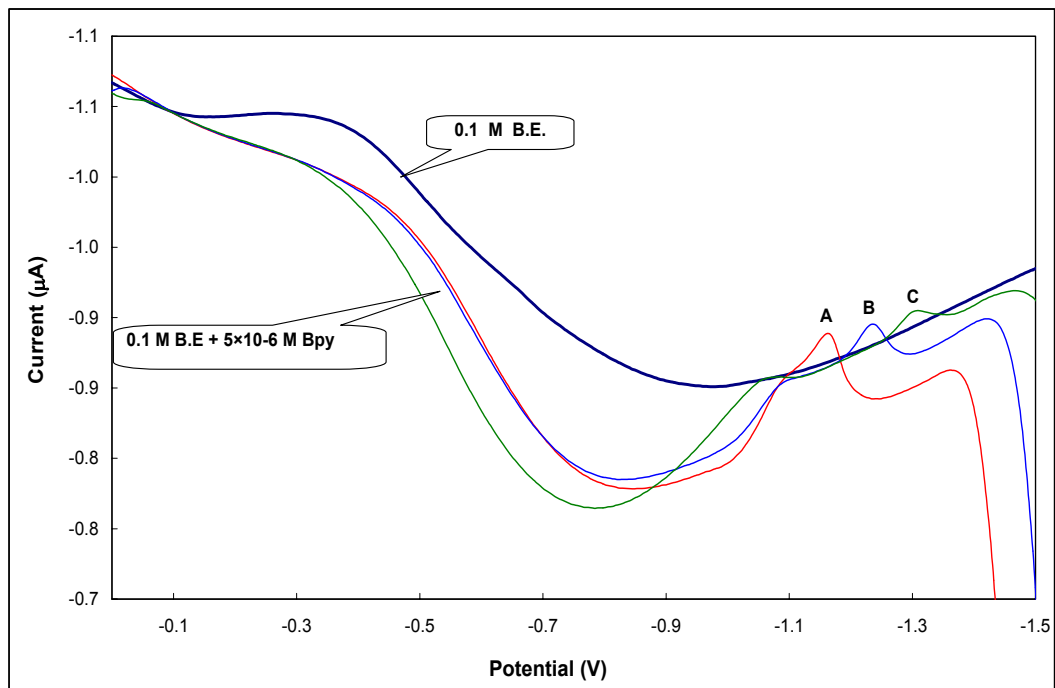


Figure 4.22: AC voltammograms of 5×10^{-6} M Bpy in 0.1 M $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ + 0.1 M NaNO_3 , pH dependence of the adsorption from A:pH 7, B: pH 8 and C: pH 9.

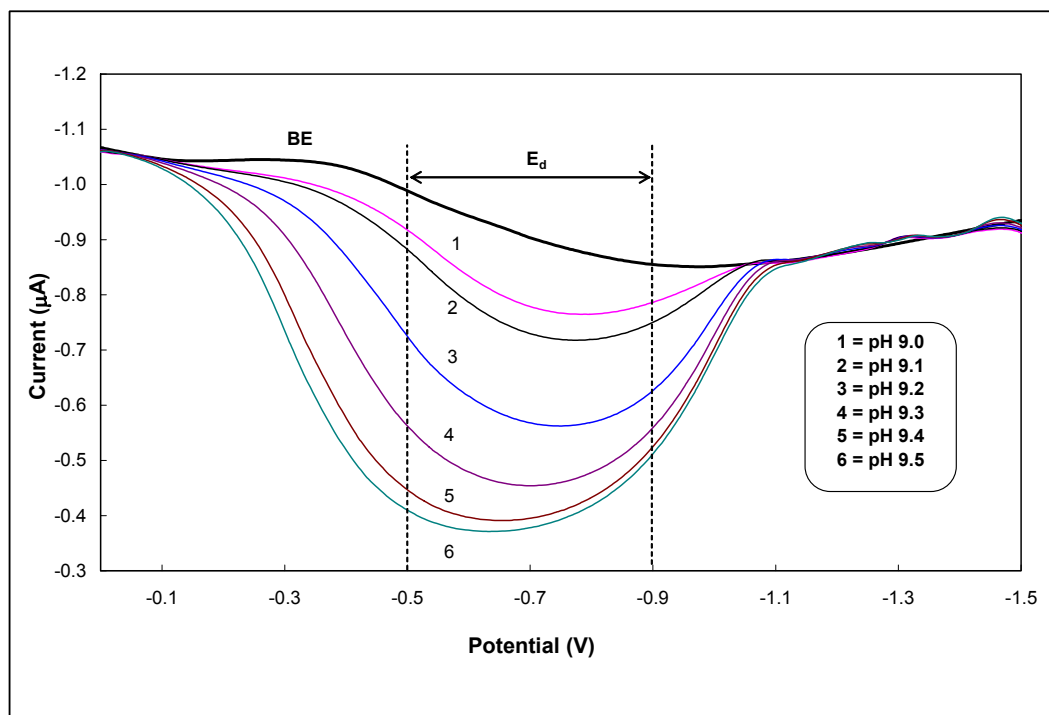


Figure 4.23: AC voltammograms of 5×10^{-6} M Bpy in 0.1 M $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ + 0.1 M NaNO_3 , pH dependence of the adsorption from pH 9 to 9.5.

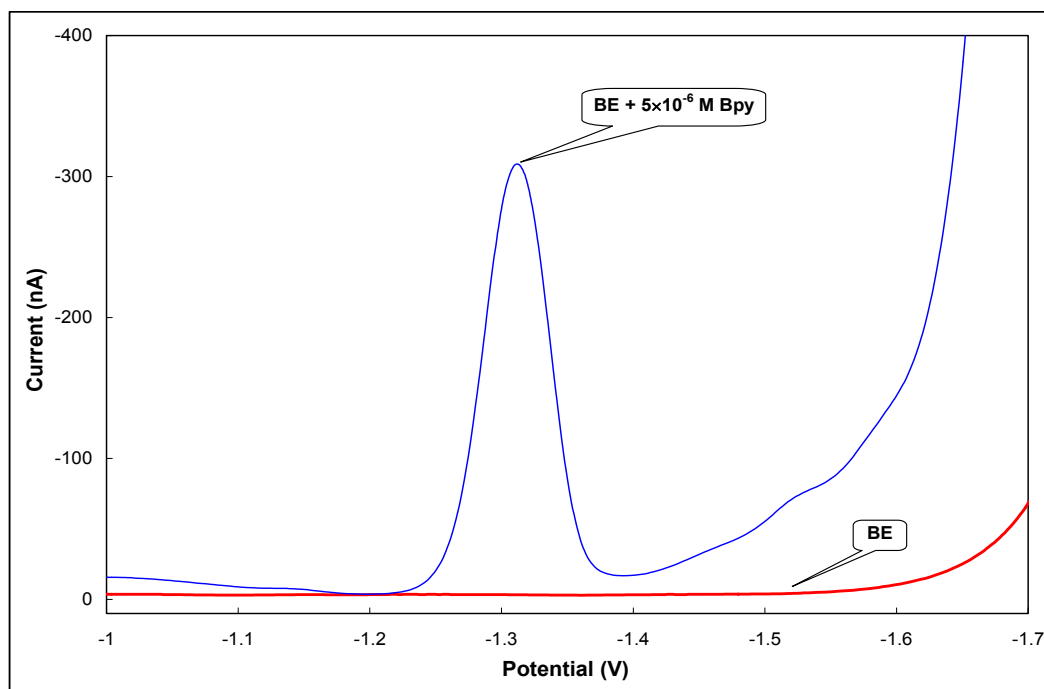


Figure 4.24: DP voltammogram of 5×10^{-6} M Bpy in 0.1 M $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ + 0.1 M NaNO_3 , pH 9. Voltage step: 0.004 V, pulse amplitude: 0.050 V, pulse time: 0.04 s, sweep rate: 0.010 V/s, HMDE used as working electrode.

AC studies of Cr^{III} -Bpy complexes

The AC behavior of the background electrolyte containing the ligand (Figures 4.18-4.20) was different when compared to the AC behavior of the Cr^{III} ion in the same electrolyte solution. The ligand showed a strong adsorption by the decrease in AC current together with a reduction peak of the ligand (Bpy) at highly negative potential. No strong evidence of chromium ions being absorbed on HMDE is observed in Figure 4.25 up to applied potential of about -900 mV. A slight change in the recorded AC voltammogram starts to be observed below -900 mV. The analysis of the CV curves seen in

Figure 4.26 was helpful in the interpretation of the AC voltammograms seen in Figure 4.25. It is clear from Figure 4.26 that the change in AC current seen in Figure 4.25 appears in the potential range where Cr^{III} is reduced in nitrate medium, most likely to Cr^{II} . Cr^{II} must have different hydrated sphere than Cr^{III} and hence the presence of $\text{Cr}^{2+}(\text{aq})_n$ at the HMDE surface will change the structure and charge density at the double layer. This, in turn, must result in a change of AC voltammogram, as it is observed in Figure 4.25 at applied potential more negative than -0.900 mV.

From experimental evidence, the ligand is strongly adsorbed onto the electrode surface. The behavior of Cr^{III} -Bpy complexes has been analyzed and according to the results obtained it appears that the complexes of Cr^{III} -Bpy are also adsorbed onto the electrode surface - see Figure 4.27. As it is seen in Figure 4.27, for the background electrolyte containing Cr^{III} and Bpy, two different peaks were recorded at pH 7. From pH 7 to 9, the first peak recorded at -0.900 mV decreased and disappeared at around pH 9, where only the second peak at -1.175 mV was recorded.

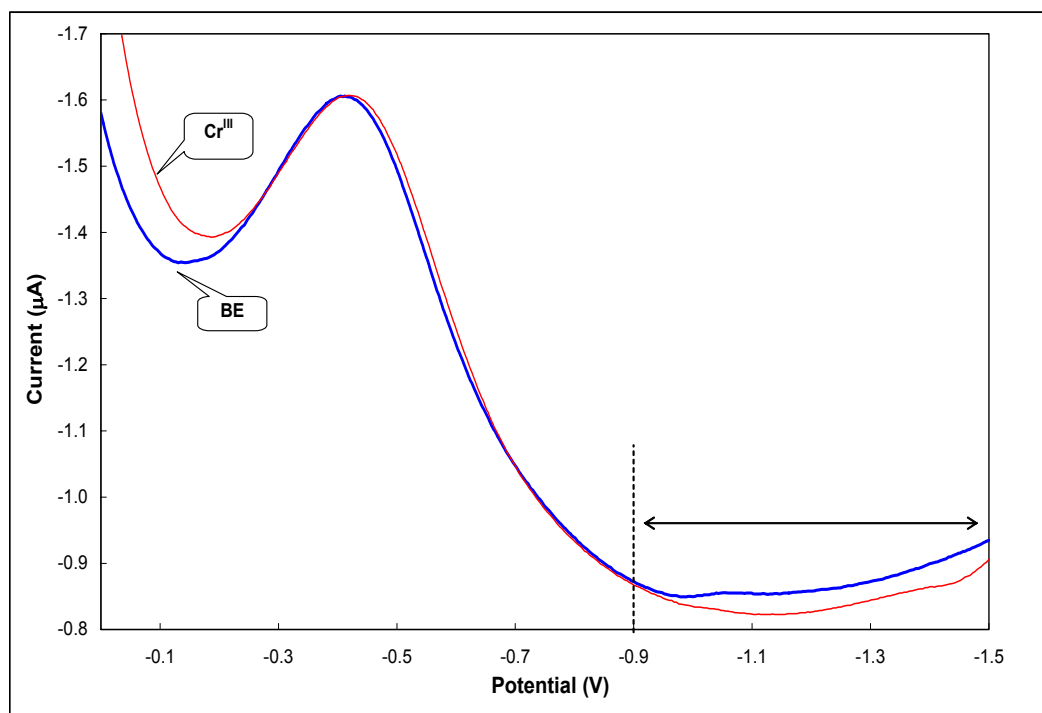


Figure 4.25: AC voltammograms of 1×10^{-4} M Cr^{III} in 0.1 M sodium nitrate of pH 5.8.

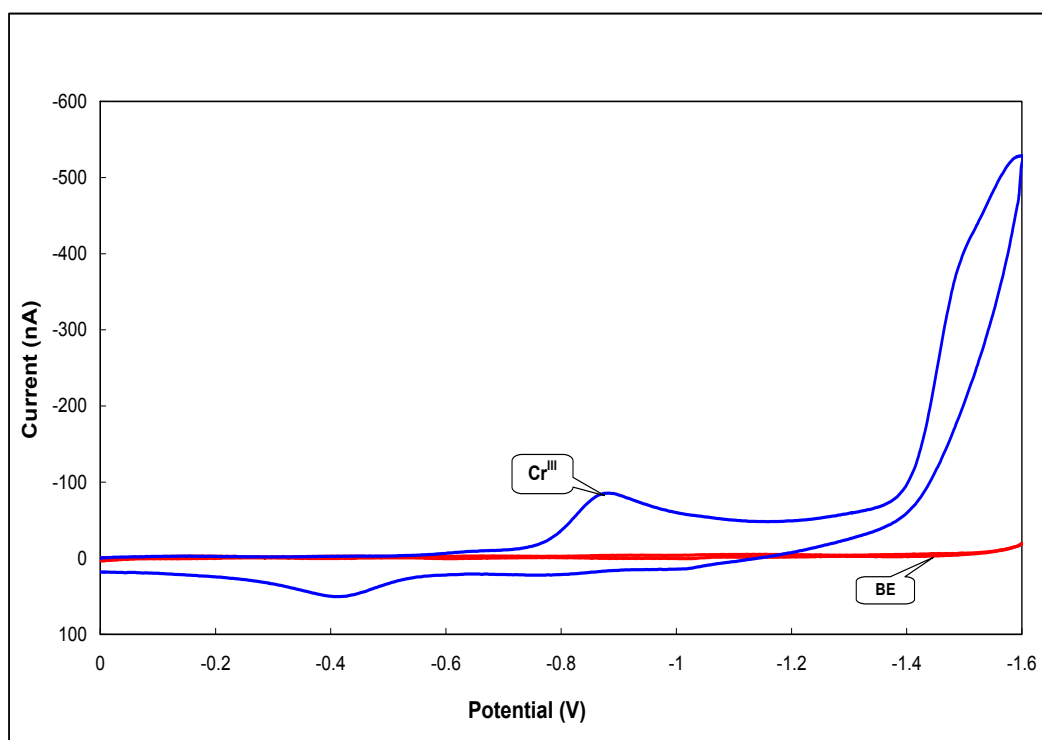


Figure 4.26: CV of 1×10^{-4} M Cr^{III} in 0.1 M sodium nitrate of pH 5.8, t_d : 30 s, E_d : -1 V, scan rate: 100 mV.

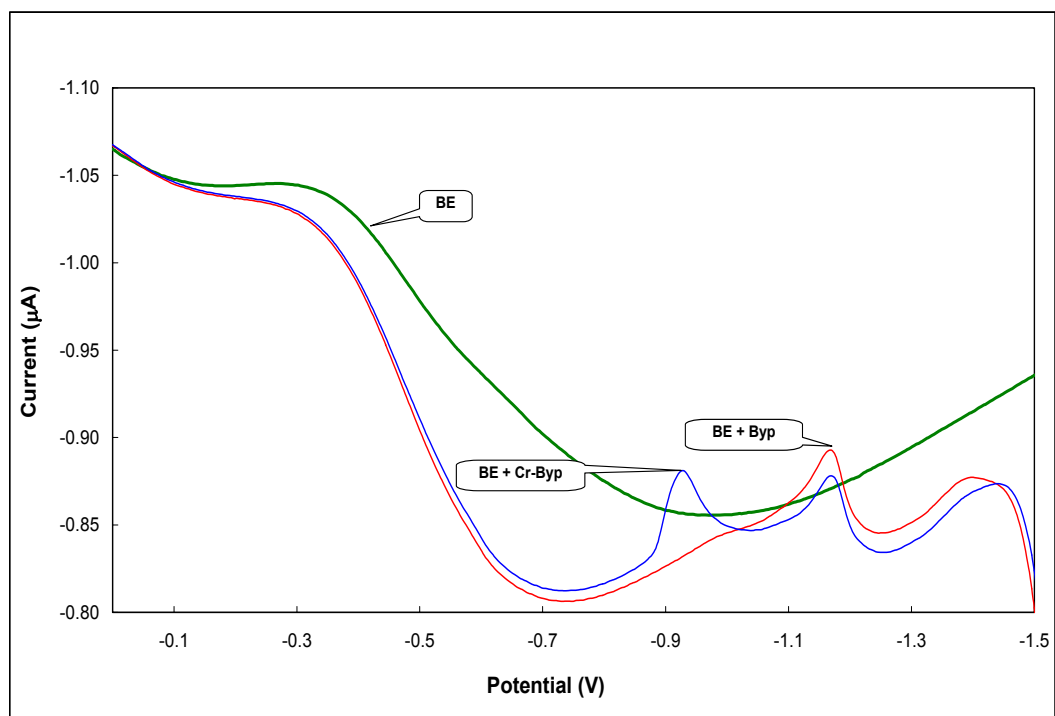


Figure 4.27: AC voltammograms comparison between the adsorption of Bpy and Cr^{III} -Bpy complexes. $L_{\text{T}} = 5 \times 10^{-6}$ M and $M_{\text{T}} = 5 \times 10^{-7}$ M; $L_{\text{T}}:M_{\text{T}} = 10$ in 0.1 M $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$, of pH 7.

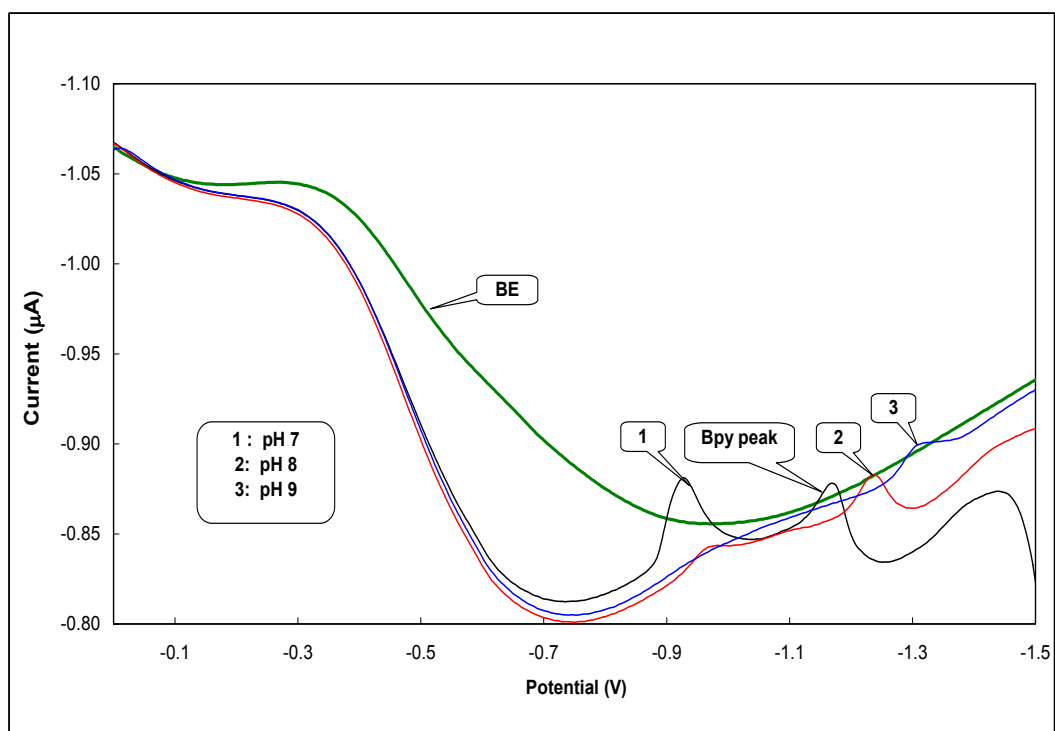


Figure 4.28: AC voltammograms of Cr^{III} -Bpy complexes. $L_{\text{T}} = 5 \times 10^{-6}$ M and $M_{\text{T}} = 5 \times 10^{-7}$ M; $L_{\text{T}}:M_{\text{T}} = 10$ in 0.1 M $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ from pH 7 to 9.

It appears that Bpy as well as Cr^{III} -Bpy complexes are stronger adsorbed at pH 7 (Figures 4.27-4.28) than the commonly used in the literature pH 9.3 [84-87] when ammonium buffer was used. Analysing the above Figures, we found that the mechanism involved in the adsorptive stripping voltammetry using Bpy can proceed according to two different ways:

- 1) It can start with the adsorption of the ligand on the electrode followed by the complexation reaction between the ligand and the metal ion,
- 2) It can also start with the complexation reaction between the ligand and the metal in the solution, followed by the adsorption of the complex onto the electrode.

Regardless on the mechanism, the final result is the same and it is that adsorbed complex (or complexes) of Cr with Bpy that are used in the AdCSV determination of Cr^{III} and Cr^{VI} .

4.2.2. CV studies of Bpy

The electrochemical reduction-oxidation process of Bpy was investigated by means of cyclic voltammetry. Bpy ligand exhibits a Quasi and Reversible process at the HMDE - see Figures 4.29-4.30. The reduction and oxidation peaks are seen in both Figures on the forward and reverse scans of the CV. In Figure 4.29, sodium nitrate was used as supporting electrolyte and the reaction involved at the electrode surface seems to be a Quasireversible one electron transfer process. In Figure 4.30, ammonium buffer was used as supporting electrolyte; the reaction of Bpy at the electrode seems to be more Reversible than in sodium nitrate. The $\Delta E = 44$ mV is narrower in Figure 4.30 when compared with 67 mV seen in Figure 4.29. This can be explained by different activity of Bpy at the electrode surface in these two supporting electrolytes. By comparing Figures 4.29-4.30 it is clear that the mid-potential (see dashed line represented by letter A at around -1.35 V) is the same for both supporting electrolytes. That indicates the appearance of the same electrochemical process at the electrode surface for both background electrolytes.

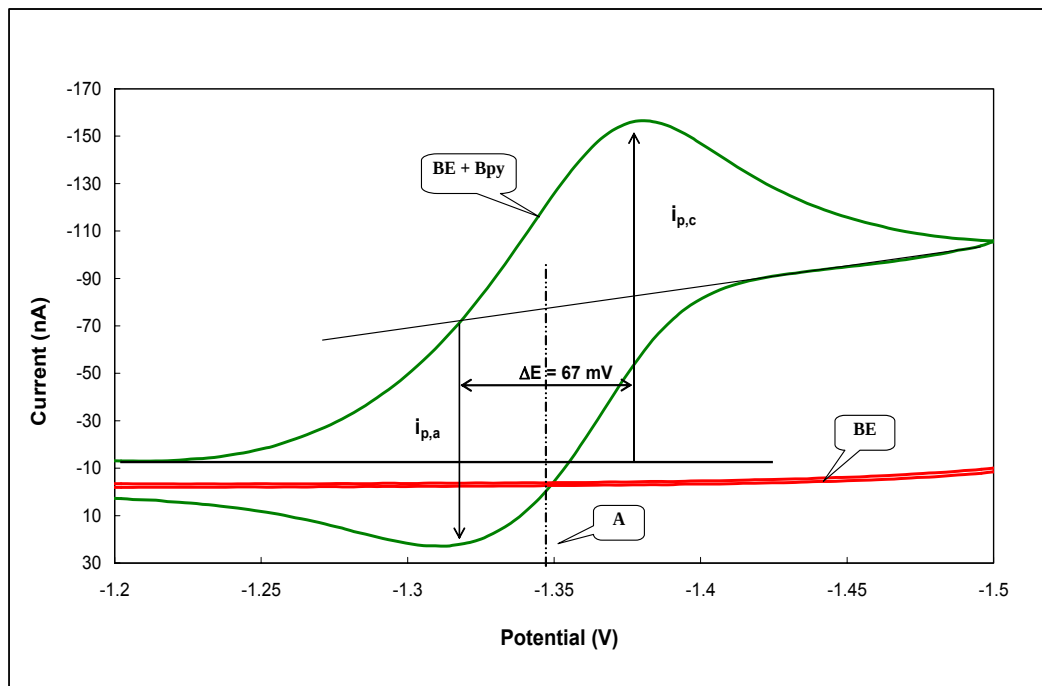


Figure 4.29: CV of 6×10^{-5} M Byp in 0.1 M NaNO_3 at pH 5.8, E_d : 0 V, t_d : 0 s, scan rate 100 mV/s. HMDE used as working electrode.

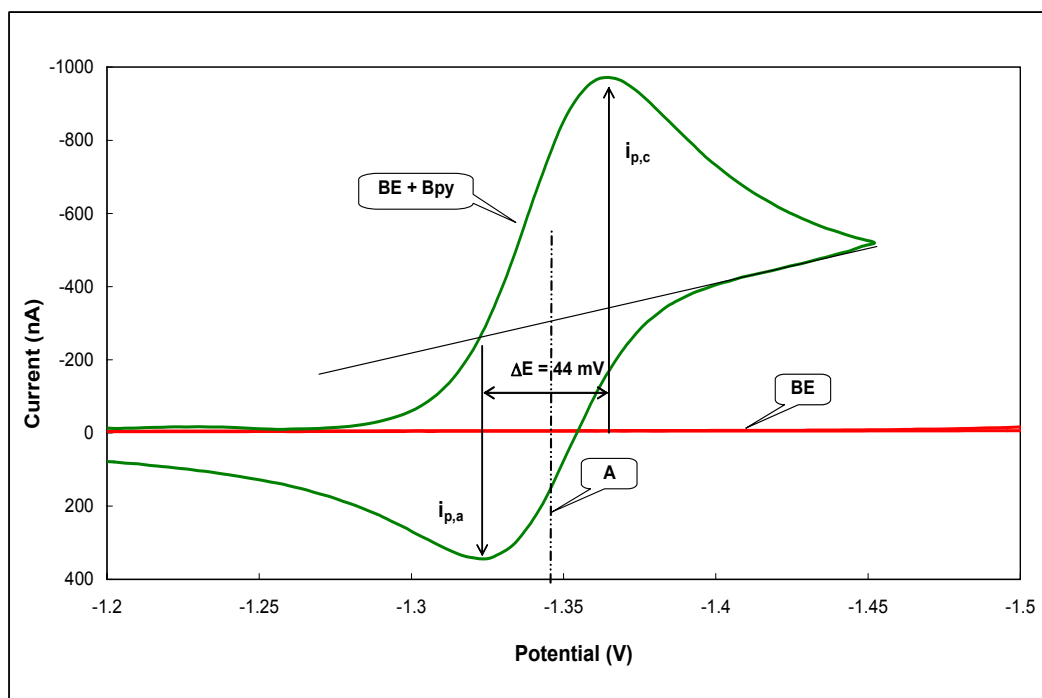


Figure 4.30: CV of 1×10^{-4} M Byp in 0.1 M $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ at pH 9. Scan rate 400 mV. HMDE used as working electrode.

CV studies of Cr^{III}-Bpy complexes

It is well known that Cr^{VI} might exist in a solution as a chromate or dichromate ions that did not form complexes with any ligand. First, in order to determine Cr^{VI} it has to be reduced to Cr^{III} and the freshly produced Cr^{III} at the electrode surface is then complexed in the presence of a ligand. The Cr^{III} ions produced at the electrode by reduction of Cr^{VI} are known to be highly reactive by producing a high signal compared to the Cr^{III} initially present in the solution. The mechanism involved at the electrode surface, when Bpy is in the presence of Cr^{III} ions is explained in Figure 4.31. The experiment has been performed at lower buffer capacity because at higher buffer capacity the reduction peaks of Bpy and chromium were overlapped. From that Figure it is quite clear that on the forward scan (i) at around -1.36 V there is a reduction peak of Bpy and (ii) the reduction of adsorbed Cr^{III}-Bpy to Cr^{II}-Bpy complex was recorded at -1.45 V. On the reverse scan oxidation current of Cr^{II}-Bpy to Cr^{III}-Bpy complex was recorded at -1.41 V followed by the reoxidation of Bpy at -1.32 V.

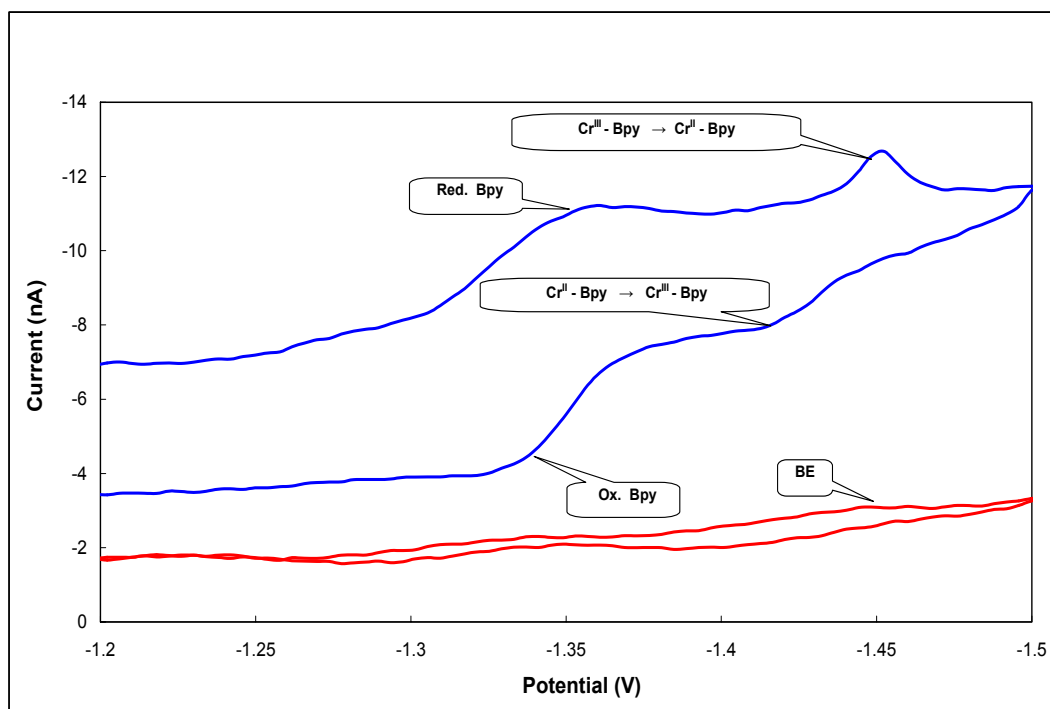


Figure 4.31: CV of 3×10^{-7} M Byp + 3×10^{-8} M Cr^{VI} in 0.003 M ammonium buffer at pH 9.3. t_d : 30 s, E_d : -1 V, scan rate 0.05 V/s. HMDE used as working electrode.

4.2.3. DP studies of Bpy

The reduction process of Bpy and Cr^{III} -Bpy complexes has been investigated by use of Differential Pulse Voltammetry. According to the species distribution diagram plotted as a function of pH (Figure 4.16) Cr^{III} -Bpy complexes were formed already at pH 2. On the basis of information provided by the species distribution diagram, we should be able to record a reduction peak of the complex at such pH values. To verify that assumption, 20 ml of 0.1 M sodium nitrate adjusted to pH 3 was used as a supporting electrolyte. The procedure employed was as follows:

- After 10 minutes of deaeration of the supporting electrolyte, a voltammogram was recorded to check the purity of the solution,
- After addition of the ligand to the supporting electrolyte and after an additional deaeration time, another voltammogram was recorded,
- Finally, after addition of the metal ion to the supporting electrolyte containing the ligand, again after an additional deaeration time, the last voltammogram was recorded.

It is seen in Figure 4.32 that a large peak at more negative potential than -1.3 V was recorded just in the supporting electrolyte at pH 3. The increases in pH from 3 to 5 resulted in the decrease of the peak and its disappearance at pH 5. From that observation it is clear that the recorded peak was related to the reduction of hydrogen ions at mercury electrode.

Upon the addition of Bpy to the supporting electrolyte at pH 3, two overlapping reduction peaks were recorded at more positive potential (Figure 4.33). The process involved at the electrode surface is a combined reduction of hydrogen ions and the monoprotonated form (HL) of the ligand, which is the predominant ligand species at pH 3 (Figure 4.3).

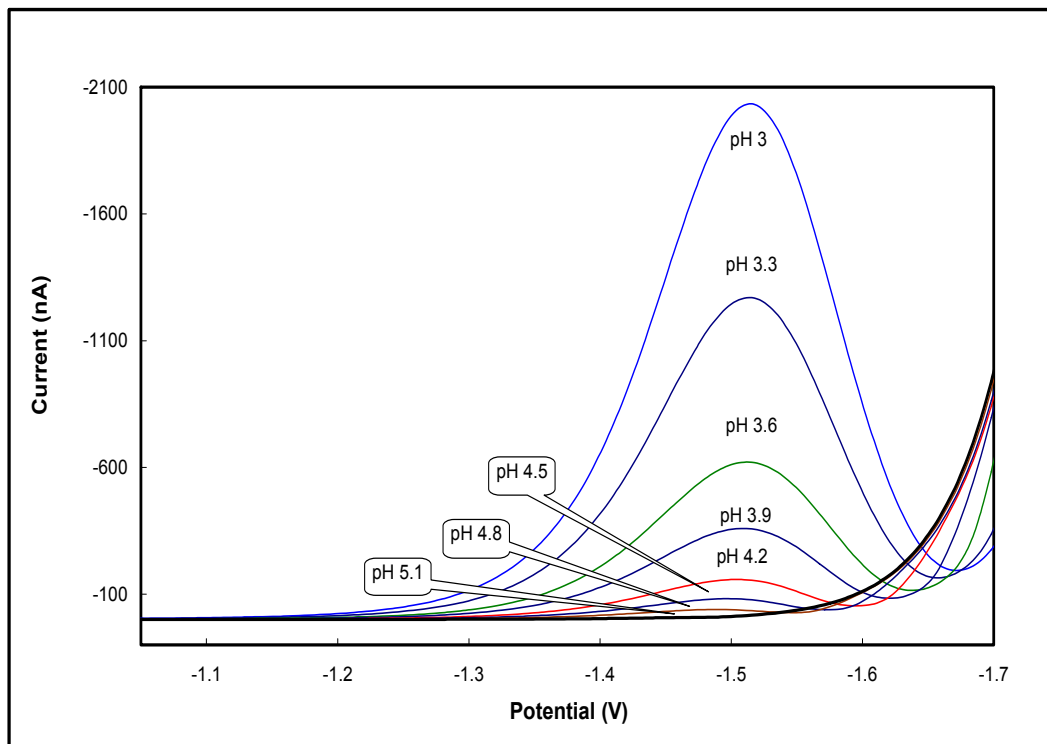


Figure 4.32: Influence of pH on DP peak of 0.1 M sodium nitrate recorded from pH 3 to pH 5.1. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

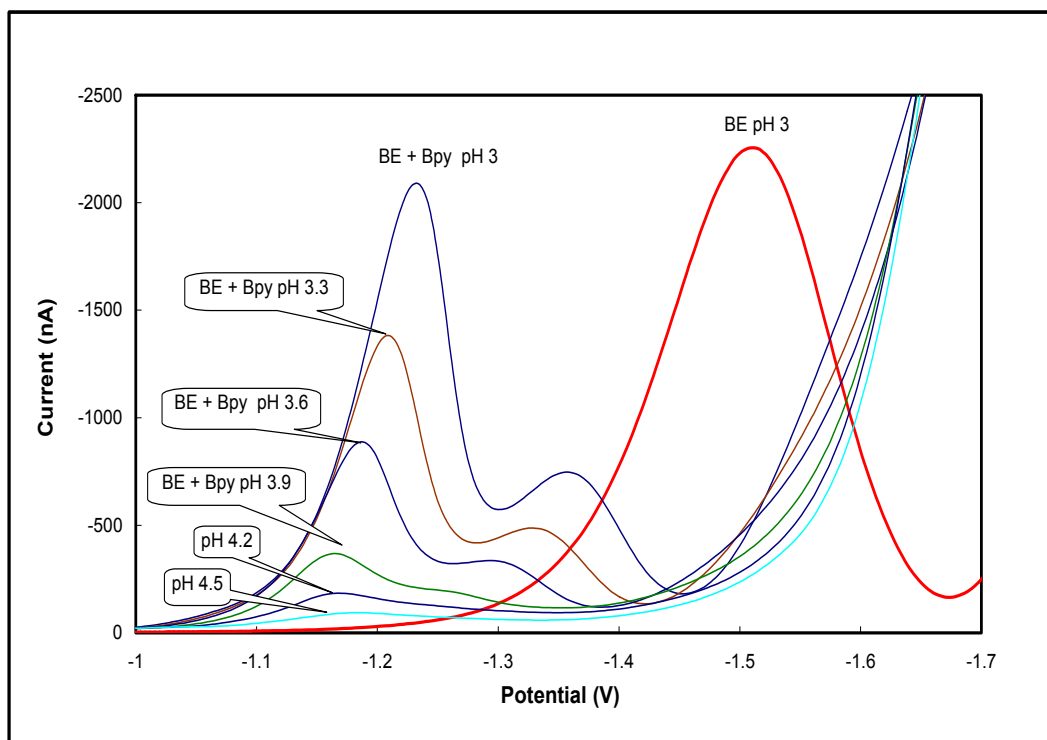


Figure 4.33: Influence of pH on DP peak of 5×10^{-6} M Bpy in 0.1 M sodium nitrate recorded from pH 3 to 4.5 t_d :30 s, E_d :-1 V. HMDE used as working electrode.

The increases of pH from 3 to 4.5 resulted in the suppression of the double peak. As shown in Figure 4.34, from pH 5.7 to 9.9 a single peak related to the presence of the deprotonated form (L) of the ligand was recorded. Within the pH range specified above, a shift of the reduction peak of Bpy together with a variation in intensity was observed from -1.26 V to -1.36 V

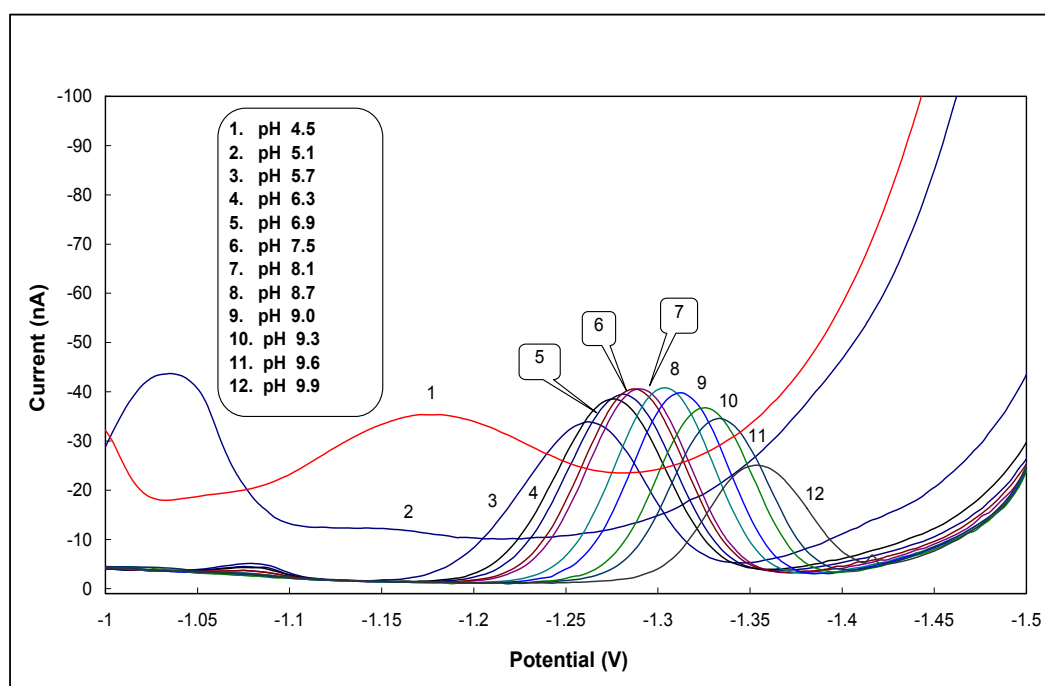


Figure 4.34: Influence of pH on DP voltammograms of 5×10^{-6} M Bpy in 0.1 M sodium nitrate recorded from pH 4.5 to 9.9.

A sharp reduction peak was recorded at -1.67 V, when the metal ion was added to the background electrolyte containing the ligand at pH 4.5 (Figure 4.35). The maximum intensity of that peak was recorded at pH 4.8. A further increase in the pH resulted in the disappearance of the reduction peak recorded at -1.67 V

and the appearance of another reduction peak at -1.45 V with a much lower current intensity when compared to the first one.

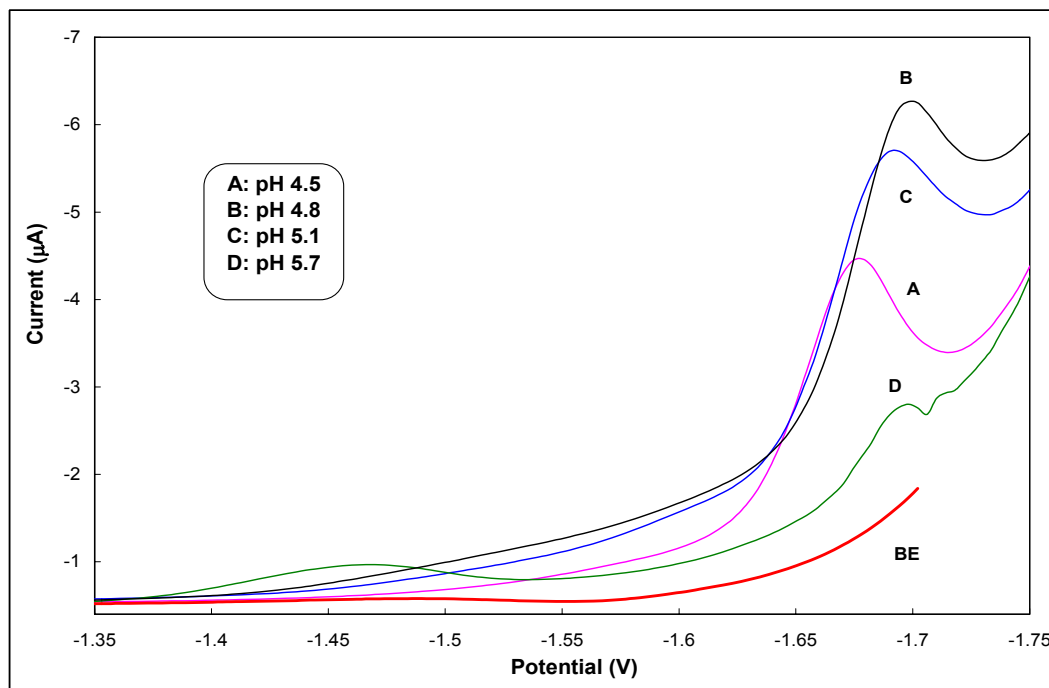


Figure 4.35: Influence of pH on DP peak of 5×10^{-6} M Byp + 1×10^{-6} Cr^{III} M in 0.1 M sodium nitrate recorded at different pH values. t_d : 30 s, E_d : -1 V, sweep rate 0.01 V. HMDE used as working electrode.

Figure 4.35 can be interpreted by comparison with the species distribution diagram plotted as a function of pH (Figure 4.16). It is clear from Figure 4.16 that the complex MLOH is the species responsible for the recorded reduction peak at -1.67 V. The maximum peak height was recorded at pH 4.8 exactly (according to Figure 4.16) where MLOH is the predominant species. A further increases in the pH resulted in a decrease of that peak. At pH 5.7 another reduction peak was recorded at -1.45 V. According to the species

distribution plot (Figure 4.16) that reduction peak is related to $ML(OH)_3$ complex. In Figure 4.36 it is quite clear that a further increases of the pH from 5.7 to 9.5 resulted in the total suppression of the peak recorded at -1.67 V (see for comparison voltammogram A and C in Figure 4.36). The peak potential shifted to more positive potential from voltammogram A to C. From that Figure one might also conclude that the peak height is also different by comparing voltammogram A with C. In reality, there is no change in the peak height. This could be easily shown by fitting an exponential background current curve to get the estimate of the peak height for both voltammograms A and C. The difference in the recorded voltammograms was essentially due to the change in the background current when pH was varied. The peak at -1.67 V recorded in the background electrolyte adjusted to pH 4.8 is most likely the catalytic reduction peak of H^+ ions on Cr^0 centres (Korolczuk [85] reported that at more negative potential than -1.5 V Cr^{III} is reduced to Cr^0). From Figure 4.37 it is clear that the reduction peak recorded at -1.67 V highly depends on the presence of chromium at the electrode surface. An increase of chromium concentration resulted in the increase of the

reduction peak recorded. In Figure 4.38, by increasing the pH to 7.5, the peak recorded at -1.67 V was totally

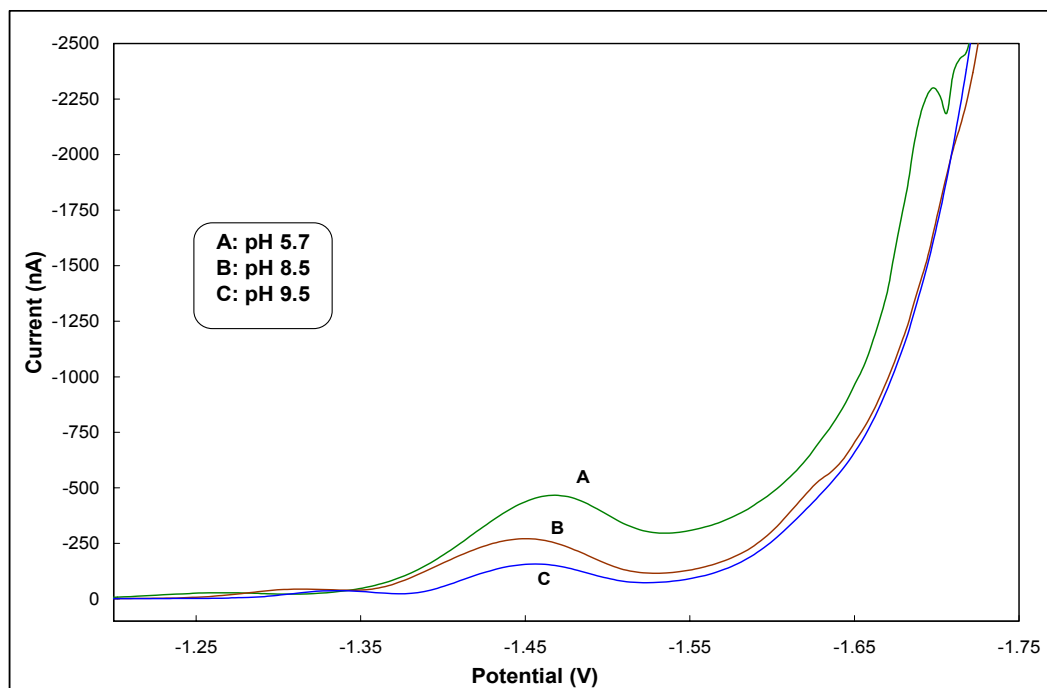


Figure 4.36: Influence of pH on DP peak of 5×10^{-6} M Byp + 1×10^{-6} M Cr^{III} in 0.1 M sodium nitrate recorded at different pH values. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

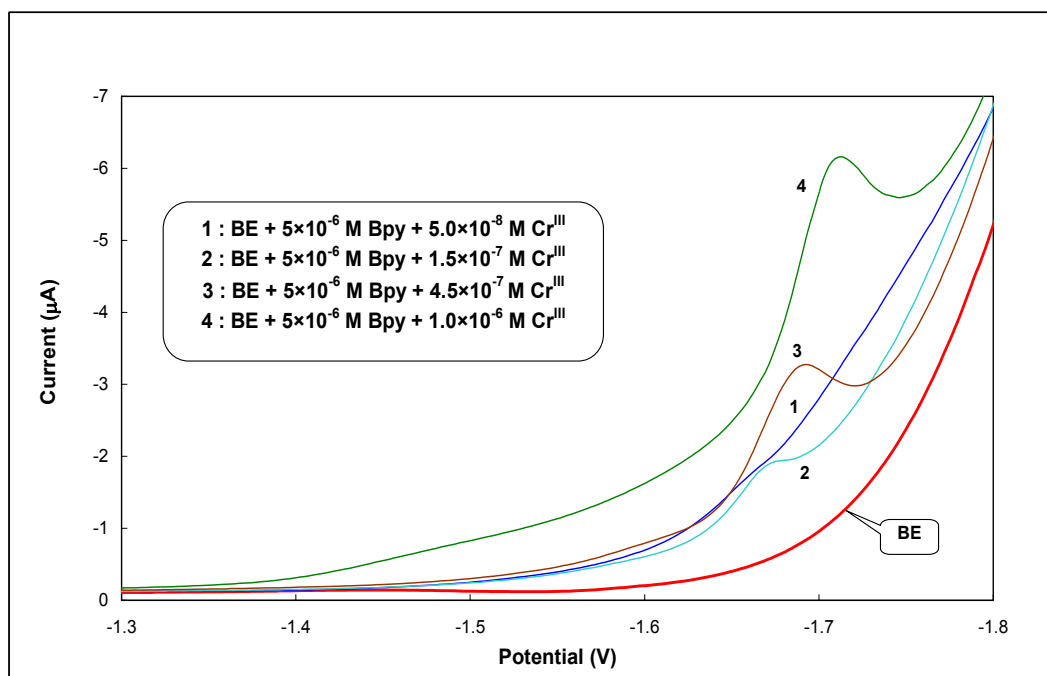


Figure 4.37: Variation of DP peaks recorded at pH 4.8 with the increase of Cr^{III} concentration. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

suppressed and another reduction peak at -1.45 V was then recorded.

By comparing the recorded voltammograms at pH 4.8 and 7.5 in Figure 4.38 it is obvious that the shape of the voltammogram at pH 4.8 showed clearly an overlapping reduction currents related to the peaks at -1.45 and -1.67 V. The shape of the reduction peak changed at pH 7.5. It has been reported that at higher concentration of the background electrolyte, an overlapping reduction phenomenon was observed [86, 121]. In Figure 4.39, to avoid that overlapping reduction phenomenon, a 0.001M NaNO₃ background electrolyte was used in order to see if we could record separate reduction peaks of Cr^{III}-Bpy complexes in the potential range from -1.45 V to -1.67 V. Four separate reduction peaks are seen in Figure 4.39. The first one, at -1.28 V, is related to the reduction of free Bpy. The reduction peaks at -1.44 and -1.53 V are related to the reduction of Cr^{III}-Bpy complexes. Finally the reduction peak at -1.67 V is related to the catalytic reduction of H⁺ ions. In Figure 4.40, a cyclic voltammogram recorded on the same solution showed clearly that the reduced species A were adsorbed onto the electrode surface. That adsorption

behaviour could be seen in the way the reduction peak was following the pattern of the background base line (see the dashed line on the voltammogram). The reduction and reoxidation of Bpy is located in the potential range between -1.30 and -1.35 V. Peak B represents diffusion controlled reduction peak of hydrogen ions on Cr^0 centres.

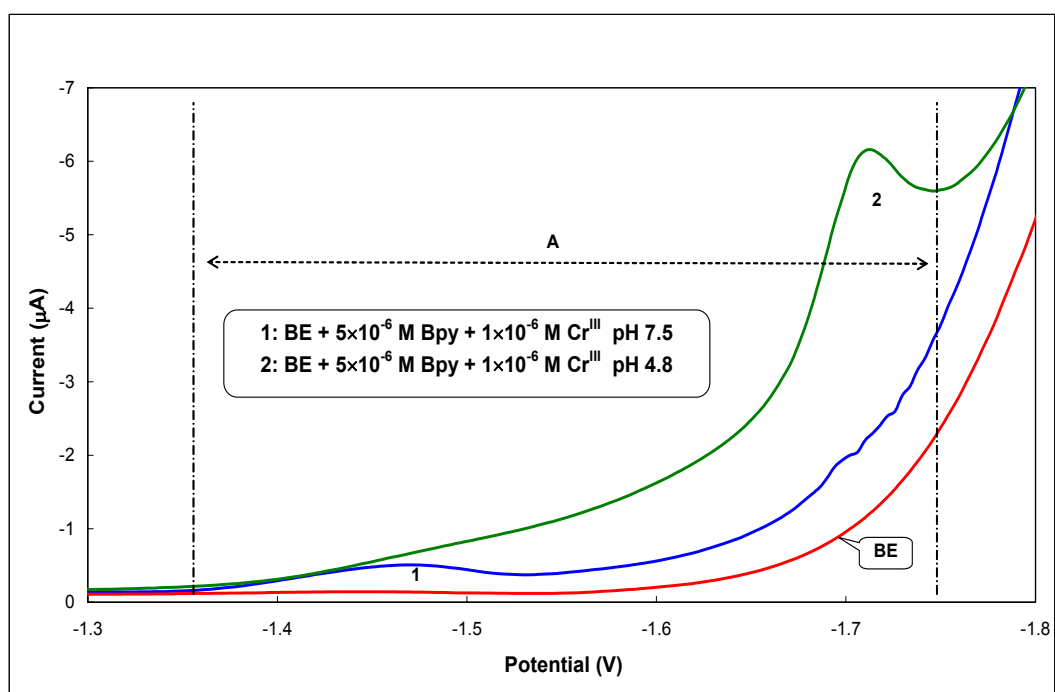


Fig. 4.38: Comparison between DP peaks of 5×10^{-6} M Byp + 1×10^{-6} Cr^{III} M in 0.1 M sodium nitrate recorded at pH.4.8 and 7.5. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

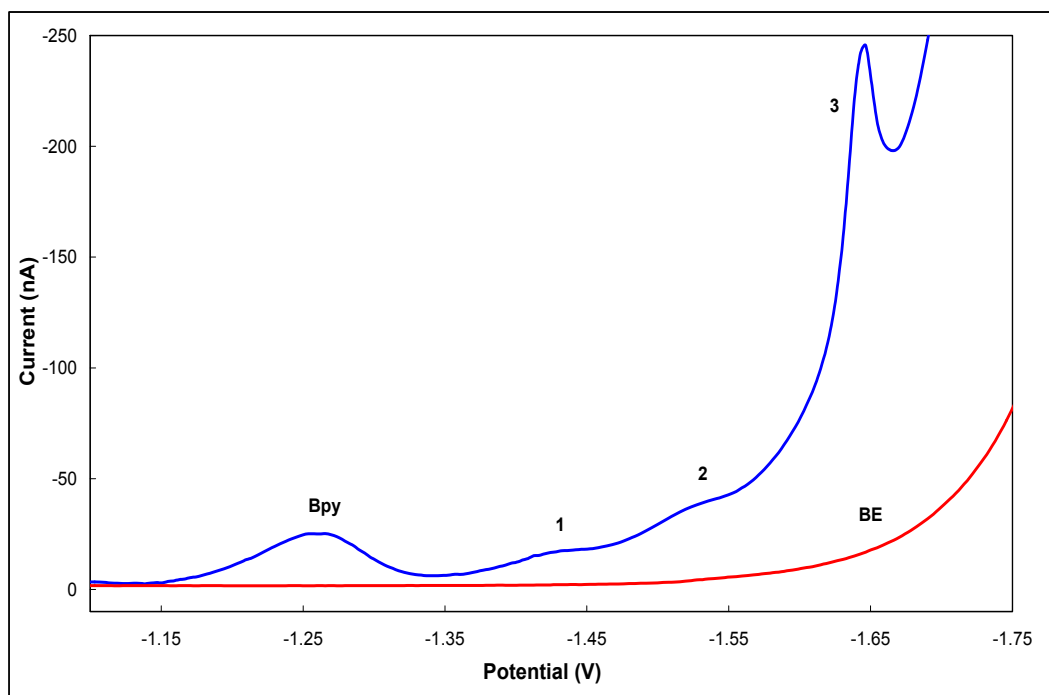


Figure 4.39: DP voltammogram of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.001 M sodium nitrate pH 7.5. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

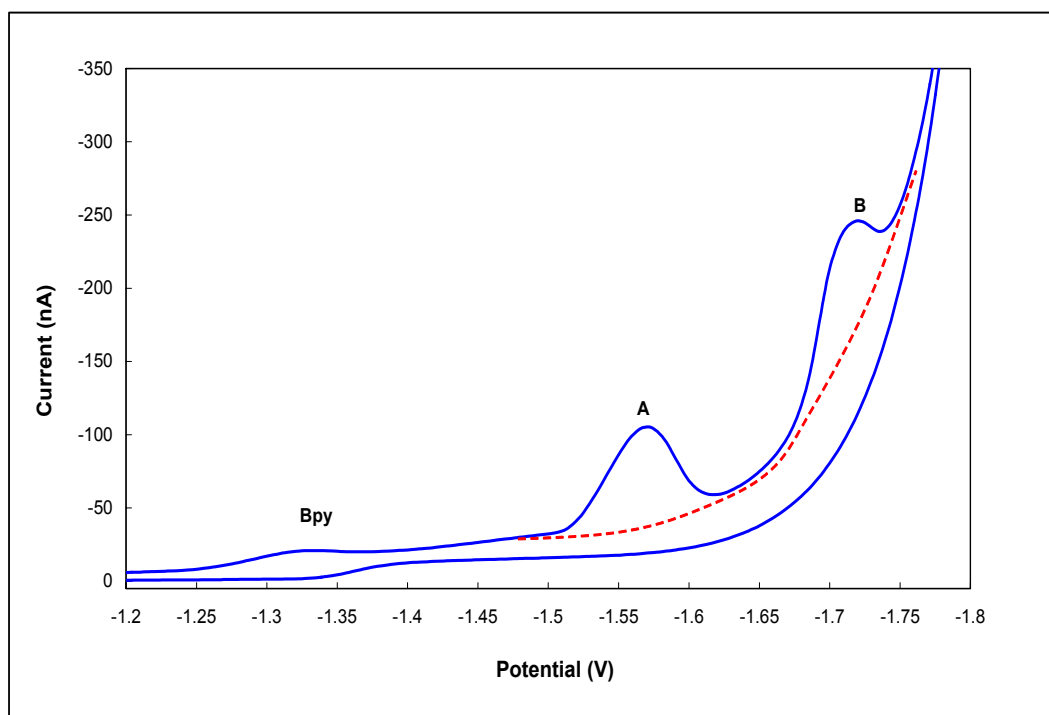


Figure 4.40: CV of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.001 M sodium nitrate pH 7.5. A: overlapping reduction of peak 1 and 2 (Figure 4.39), B: reduction of H^+ on Cr^0 . t_d :30 s, E_d :-1 V, scan rate 0.05 V/s. HMDE used as working electrode.

4.2.4. Optimization of analytical procedures

The reported analytical procedures involving Bpy were optimised for environmental materials [84] and natural waters [85, 87]. The optimised procedures were only focused on the peak recorded at -1.45 V in the high pH region and ammonium buffer at pH 9.3 was used as supporting electrolyte. In this work sodium nitrate was used as supporting electrolyte and some analytical parameters such (interfering metal ions, deposition time, catalytic effect of nitrate ions and ligand concentration) were optimised for low and high pH values. Two kinds of procedures could be developed. The first one can monitor the peak recorded at pH 4.8 and the second one can monitor the peak recorded at higher pH values.

A. Interpretation of interfering metals

Competition between metal ions to form complexes with a ligand occurs in a solution. Three metal ions Zn, Co and Ni were selected for investigation. Zinc was selected because it is an ion commonly found in water and does exist as a trace metal in most chemicals. Cobalt and nickel were selected because it was reported by Gao and Siow [84] that, they both interfere strongly with the reduction peak of Cr^{III} -Bpy. The interference

was studied for both pH values (4.8 and 7.5) with the purpose to see which one of these two recorded reduction peaks was more affected.

The results obtained in the presence of zinc showed that the reduction peak of Cr^{III} -Bpy recorded at -1.45 V (pH 7.5) was more strongly affected than the one recorded at -1.67 V (pH 4.8). The reduction peak recorded at pH 7.5 was totally suppressed at zinc concentration higher than 2 μM ($[\text{Zn}]:[\text{Cr}]$ ratio = 4) – see Figures 4.41-4.42.

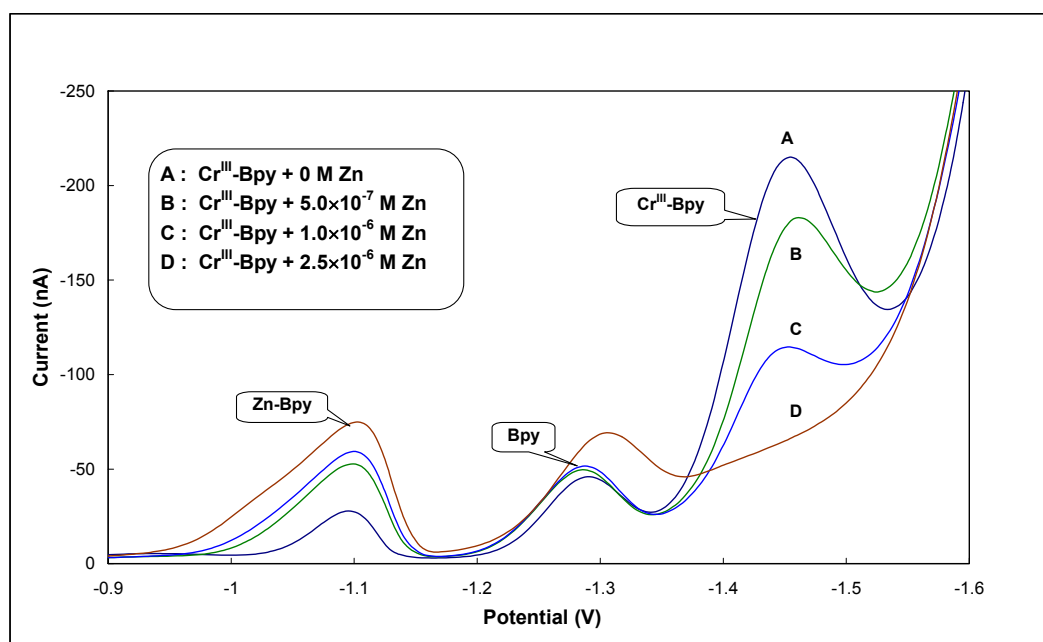


Figure 4.41: DP voltammograms of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 7.5. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

The reduction peak recorded at -1.67 V (pH 4.8), known as a catalytic reduction of H^+ ions on metallic chromium centres was also affected by the presence of

Zn ion, but not as much as the reduction peak recorded at -1.45 V (pH 7.5).

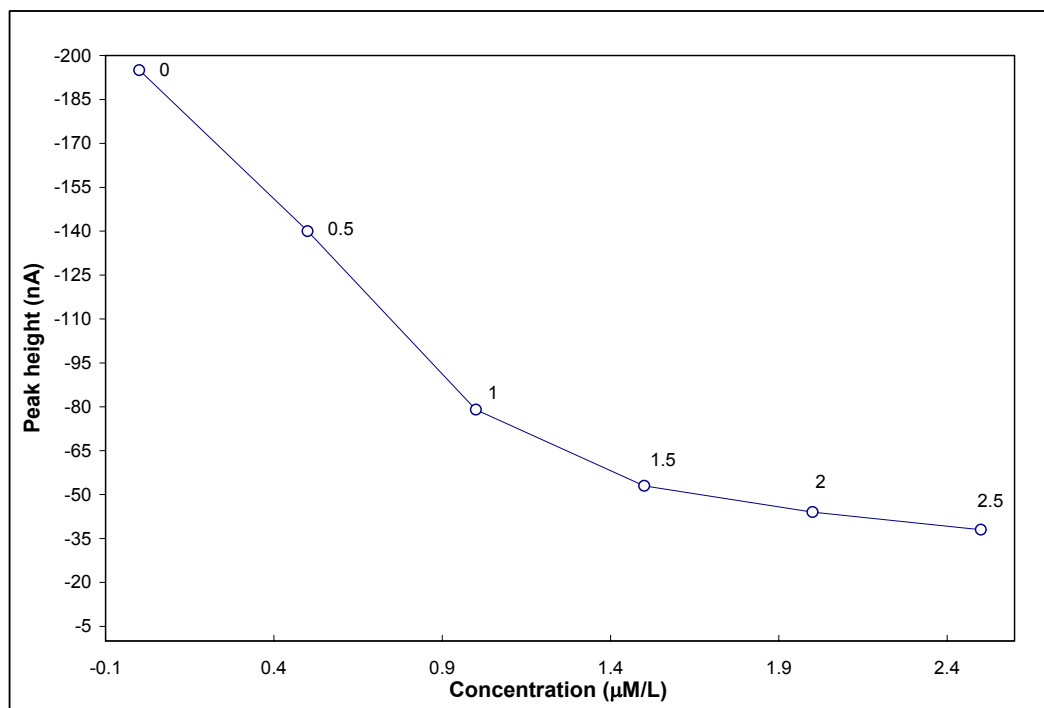


Figure 4.42: Variation of the peak height of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 7.5 as zinc concentration increases.

At zinc concentration equal to 14 μM at pH 4.8 ([Zn]:[Cr] ratio = 28, seven times more zinc concentration when compared with the previous case), even if the peak height decreased, there was still a possibility to monitor that catalytic hydrogen reduction peak. That peak could be preferred for analytical purpose because it allows monitoring of chromium in the presence of high zinc concentration (Figures 4.43-4.44).

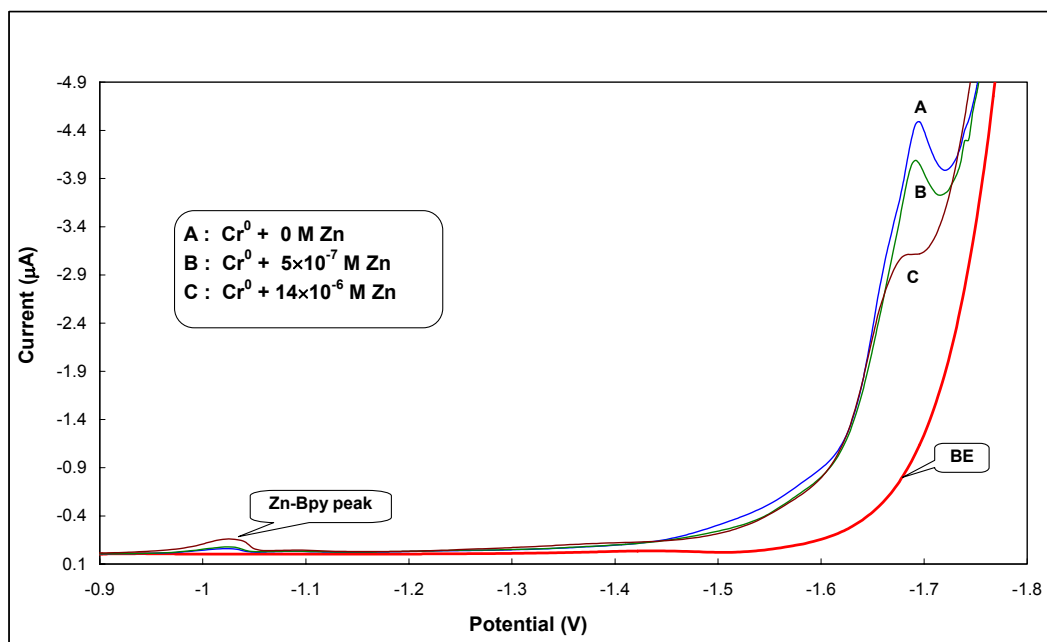


Figure 4.43: DP voltammograms of $5 \times 10^{-6} \text{ M Byp} + 5 \times 10^{-7} \text{ M Cr}^{\text{III}}$, in 0.1 M sodium nitrate pH 4.8, at different zinc concentrations. t_d : 30 s, E_d : -1 V. HMDE used as working electrode.

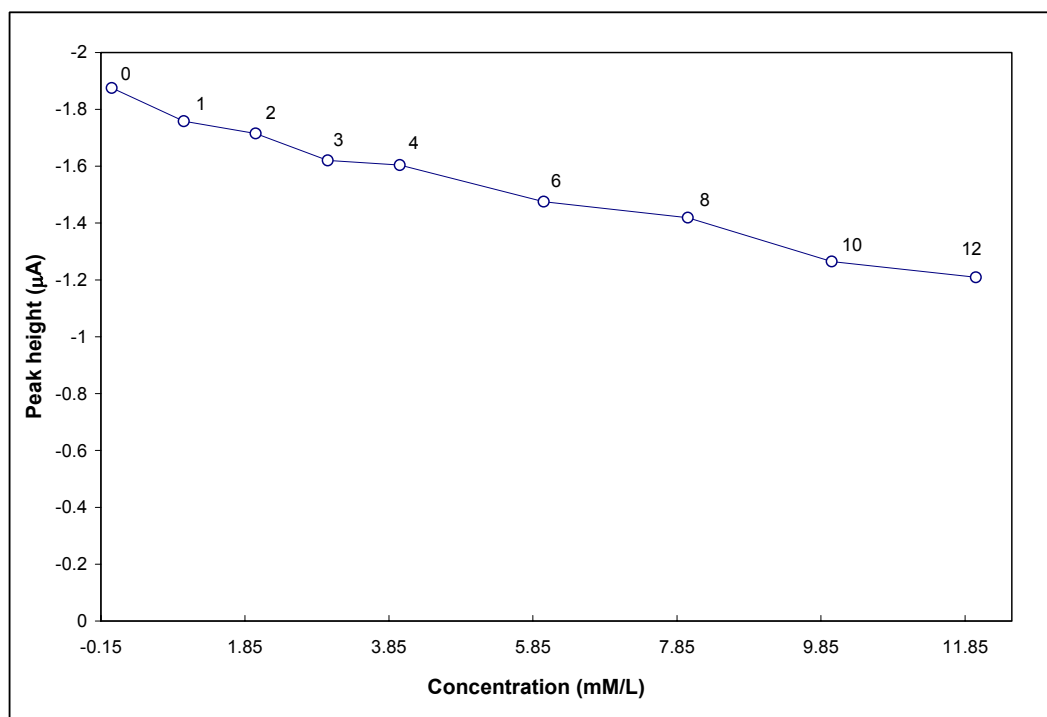


Figure 4.44: Variation of the peak height of $5 \times 10^{-6} \text{ M Byp} + 5 \times 10^{-7} \text{ M Cr}^{\text{III}}$, in 0.1 M sodium nitrate pH 4.8 as zinc concentration increases.

In Figures 4.45-4.46 cobalt ions showed a strong interference on the catalytic H^+ reduction peak

recorded at -1.67 V. At lower pH, the addition of cobalt, at the same concentration then chromium ($[\text{Co}]:[\text{Cr}]$ ratio = 1), resulted in a big change in the shape of the voltammogram and a disappearance of the reduction peak at -1.67 V. That change can be interpreted as a combined process of the catalytic reduction of hydrogen on Cr and Co onto the electrode surface. Cukrowski and Havel [119, 120] used Artificial Neural Network (ANN) in the evaluation of electrochemical data for fully inert and dynamic metal complexes and estimated the stability constants.

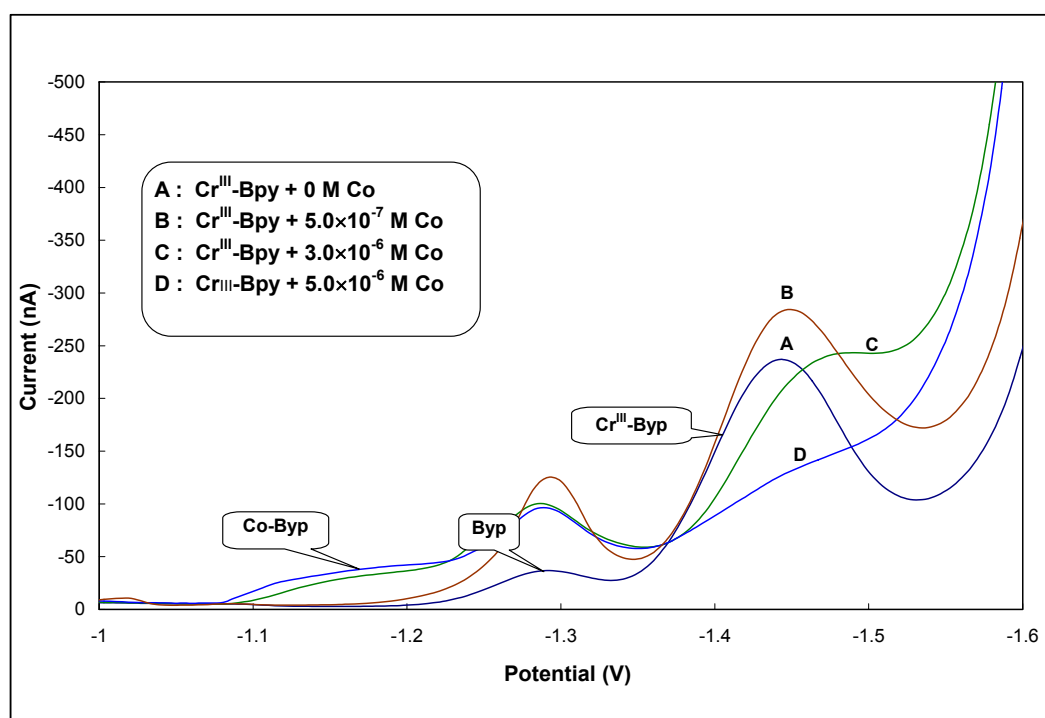


Figure 4.45: DP voltammograms of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III}, in 0.1 M sodium nitrate pH 7.5. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

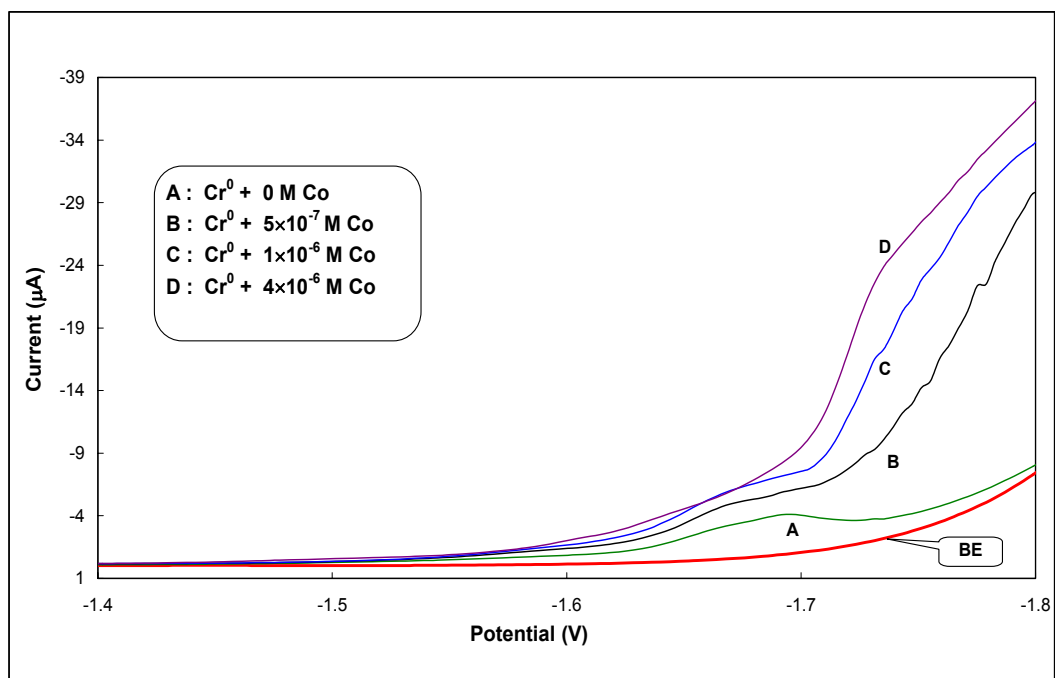


Fig.4.46: DP voltammograms of 5×10⁻⁶ M Byp + 5×10⁻⁷ M Cr^{III}, in 0.1 M sodium nitrate pH 4.8 t_d :30 s, E_d :-1 V. HMDE used as working electrode.

In the present case ANN could be used in the evaluation of that combined behavior of hydrogen reduction on chromium and cobalt deposits. This could be used for the simultaneous determination of chromium and cobalt in a sample.

In the presence of nickel (Figures 4.47-4.48) the reduction peak of Cr^{III}-Bpy recorded at pH 7.5 was strongly affected when compared to the catalytic reduction peak of hydrogen recorded at pH 4.8 (Figures 4.49-4.50). The addition of nickel ion to the cell resulted in an increase of the peak height initially and then a decrease in the peak height was observed as nickel concentration increases (Figures 4.47-4.48).

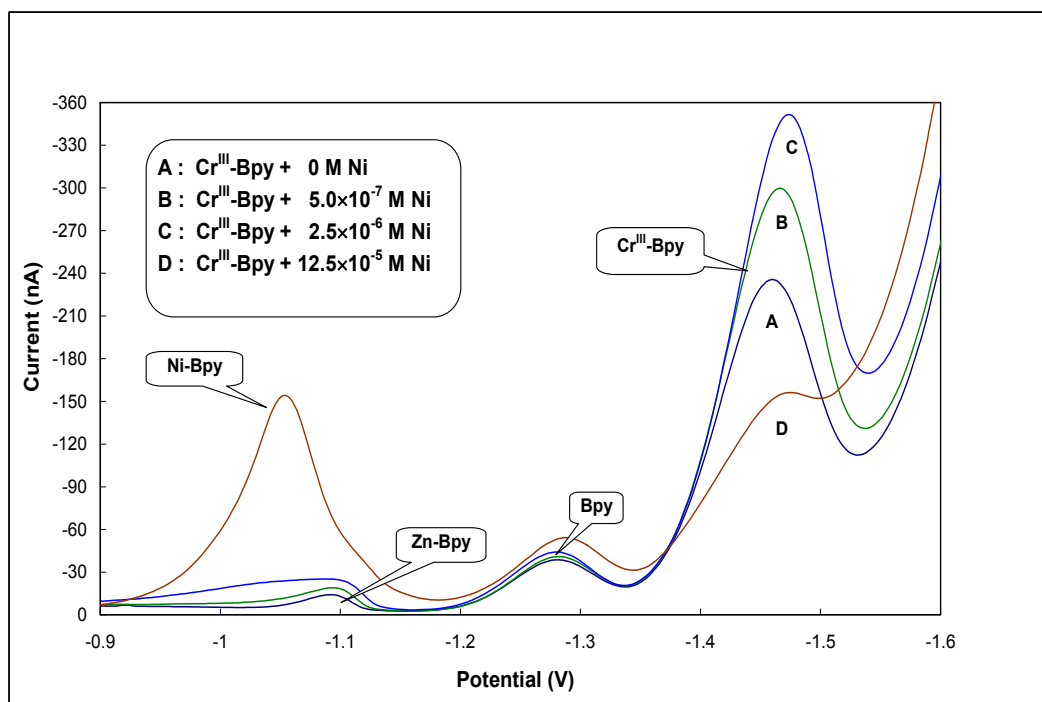


Figure 4.47: DP voltammograms of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 7.5. t_d : 30 s, E_d : -1 V. HMDE used as working electrode.

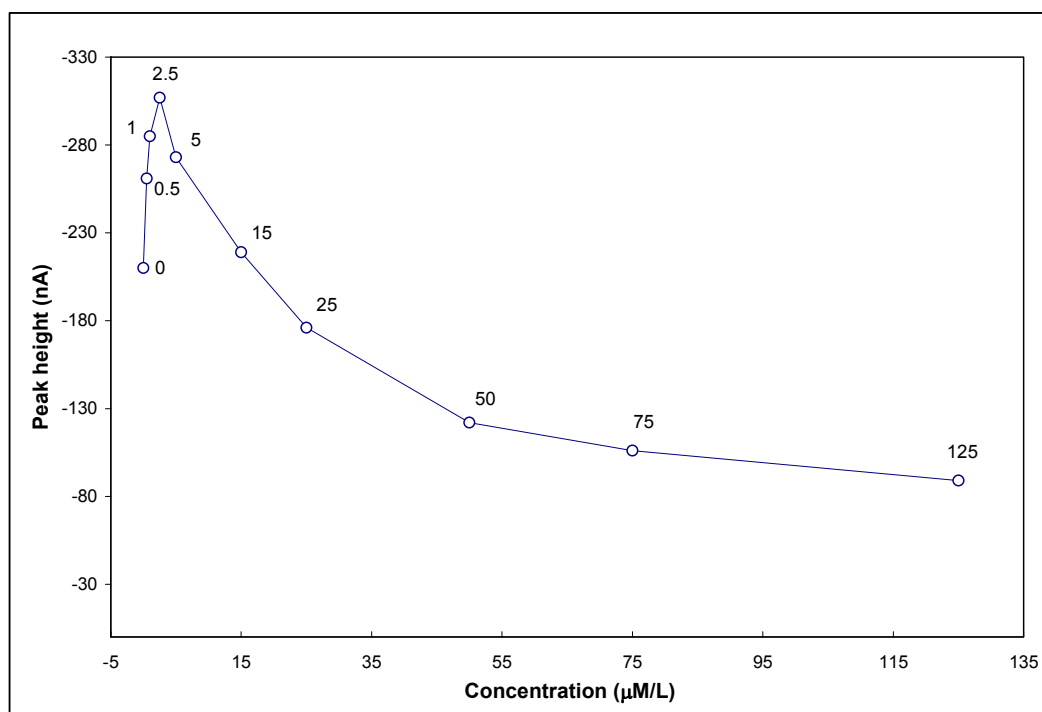


Figure 4.48: Variation of the peak height of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 7.5 as nickel concentration increases.

The catalytic reduction peak of hydrogen recorded at -1.67 V was less affected when compared to the reduction peak of Cr^{III} -Bpy recorded at -1.45 V (Figures 4.49-4.50). After the addition of nickel ion, initially again an increase in the peak height was observed then followed by the decrease in the peak height. At concentration larger than 10 μM of nickel, the peak height remained almost constant; any further increase of nickel concentration did not affect the peak height.

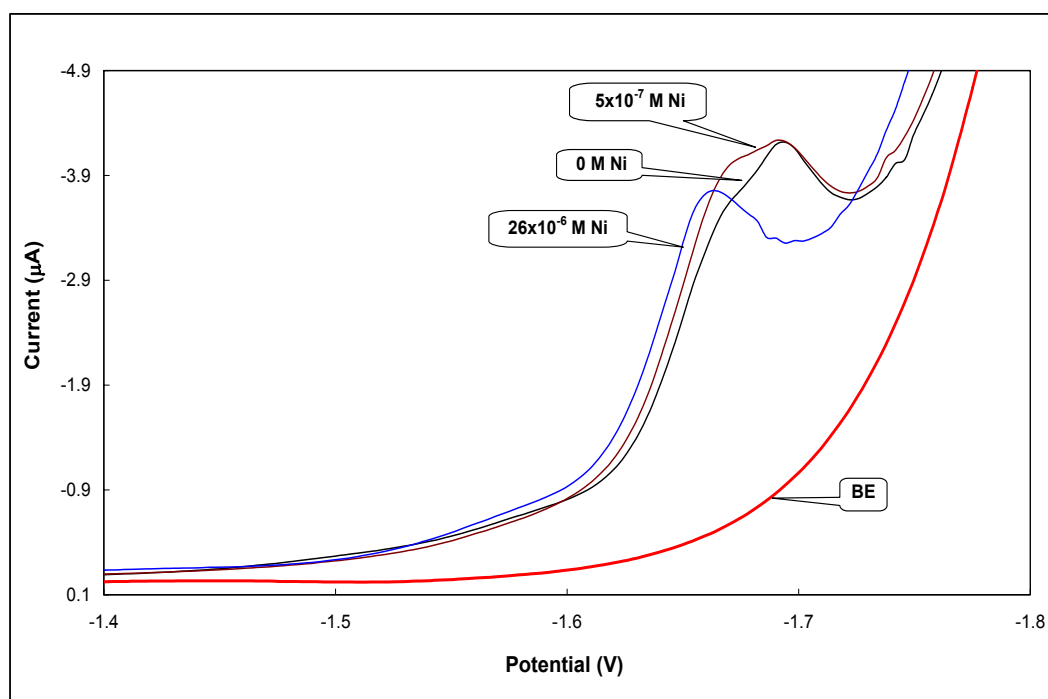


Figure 4.49: DP voltammograms of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 4.8. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

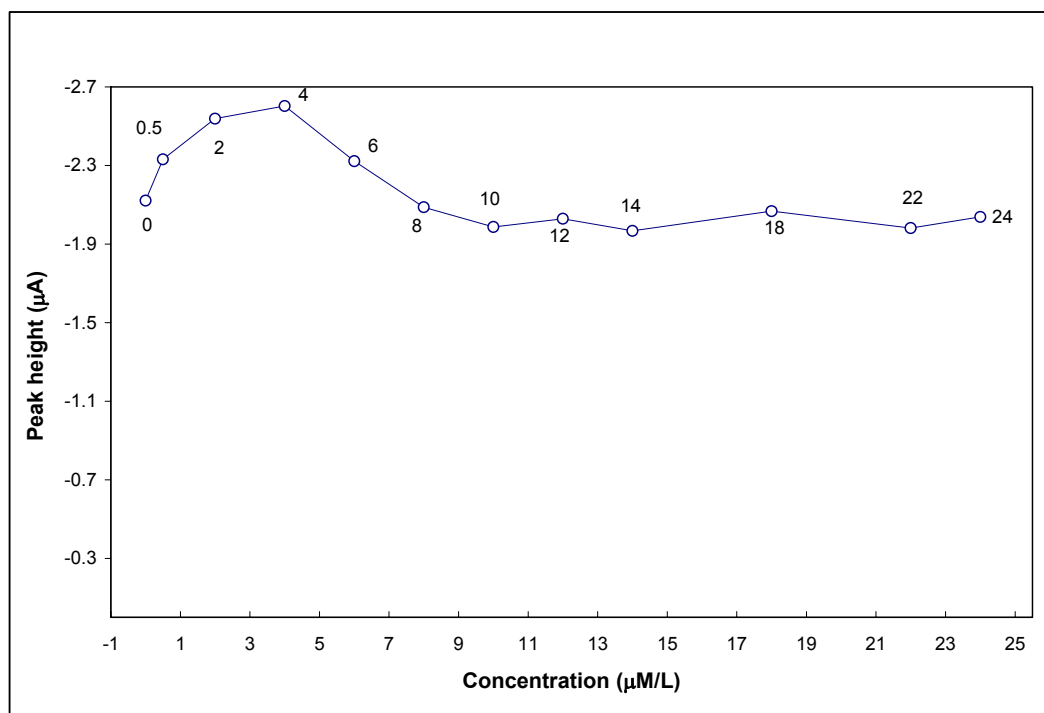


Figure 4.50: Variation of the peak height of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 4.8 as nickel concentration increases

It has been reported by Gao and Siow [84] that cobalt and nickel interfere strongly with the determination of chromium. As reported by Gao and Siow they both produce a catalytic reduction peak with a similar peak potential to that of chromium. In this work, according to the experimental evidences, cobalt and nickel did not produce any catalytic reduction peak similar to the one recorded for chromium (Figures 4.45, 4.47, 4.51 and 4.52). From these figures it can be seen that both in sodium nitrate and ammonium buffer supporting electrolytes, Co and Ni are reduced at more positive potential compared with Cr^{III} -Bpy complexes. In Figure 4.53 the behavior of cobalt and nickel alone in the

presence of Bpy in 0.1 M sodium nitrate at pH 4.8 was also investigated. The results showed that neither nickel nor cobalt did produce any catalytic hydrogen reduction peak at -1.67 V as recorded for Cr.

From that evidence it is clear that the increases in the peak height upon the addition of Co and Ni metal ions may be due to some unknown combined reactions occurring at the working electrode. Further investigations are needed to clarify that unique behaviour recorded in this work, it was also reported earlier by Gao and Siow [84] but without a clear solution to it.

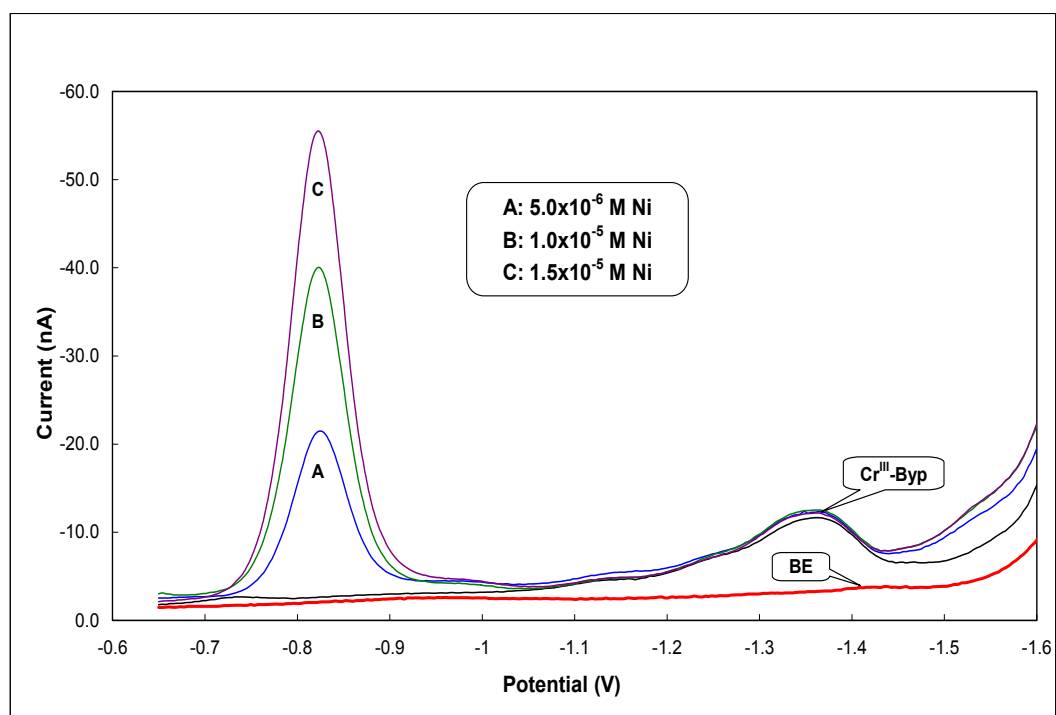


Figure 4.51: DP voltammograms behaviour of 1×10^{-7} M Byp + 1×10^{-8} M Cr^{III} in 0.1 M ammonium buffer at pH 9.3 with different Ni concentration. t_d : 30 s, E_d : -1 V. HMDE used as working electrode.

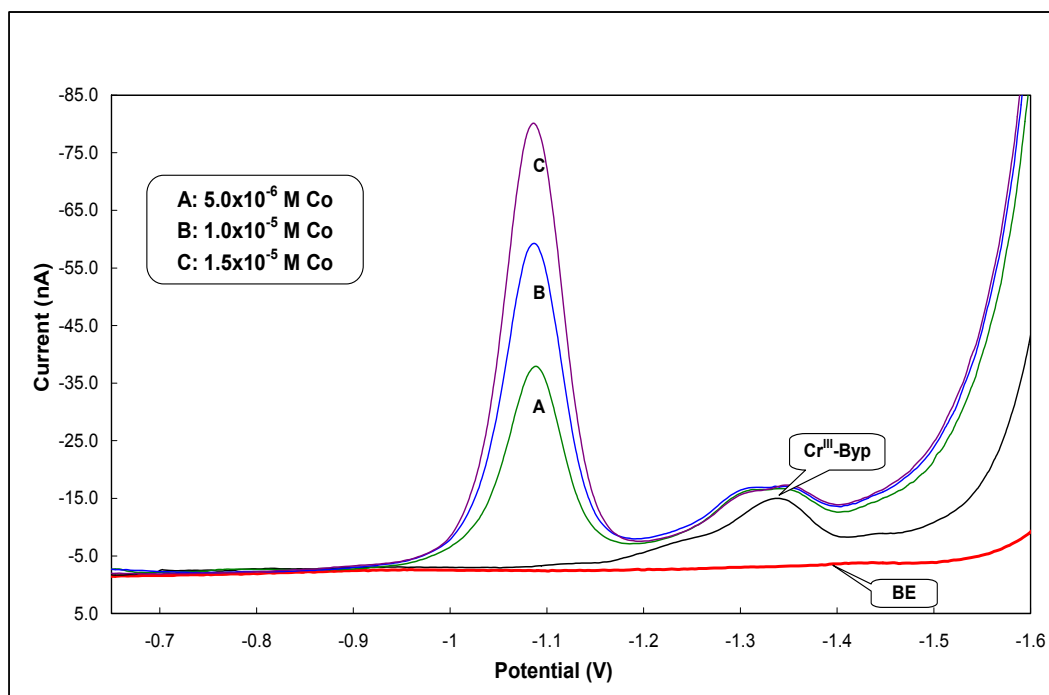


Figure 4.52: DP voltammograms behaviour of 1×10^{-7} M Byp + 1×10^{-8} M Cr^{III} in 0.1 M ammonium buffer at pH 9.3 with different Co concentration. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

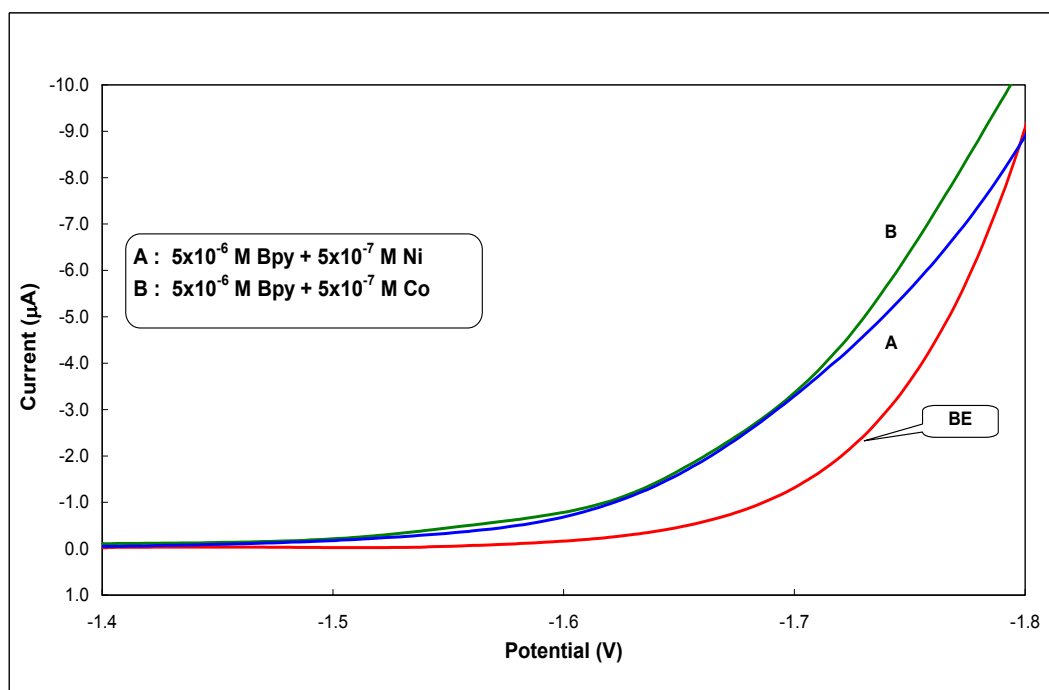


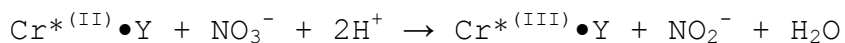
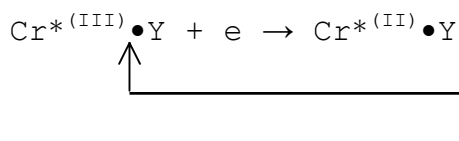
Figure 4.53: DP voltammograms of 5×10^{-6} M Byp + 5×10^{-7} M Co and 5×10^{-7} M Ni in 0.1 M sodium nitrate pH 4.8. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

B. Influence of nitrate concentration on chromium peak height

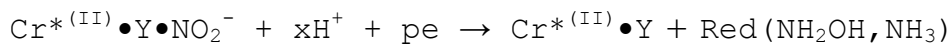
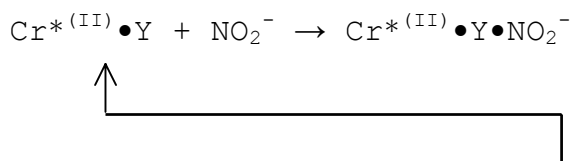
In catalytic adsorptive stripping voltammetry (AdCSV), high sensitivity of the voltammetric signal can be achieved using catalytic systems. In chromium determination and speciation both nitrate and nitrite were used as catalytic agents [78-99].

Bobrowski and Zarebski [121] proposed a reaction scheme of the catalytic reaction between the redox pair $\text{Cr}^{\text{III}}/\text{Cr}^{\text{II}}$. The mechanism was reported to occur in two steps:

1) At a more positive potential:



2) At a more negative potential:



Where $\text{Cr}^{*(\text{II})}\bullet\text{Y}$ is in situ formed active complex [121].

Both nitrate and nitrite are used as catalytic agent in chromium determination and speciation. In Figure 4.54 there is a comparison between the catalytic effect of

nitrate and nitrite. For both curves, an exponential background was used for the estimation of the peak height. Both nitrite and nitrate have good catalytic effect on the determination of Cr^{III} .

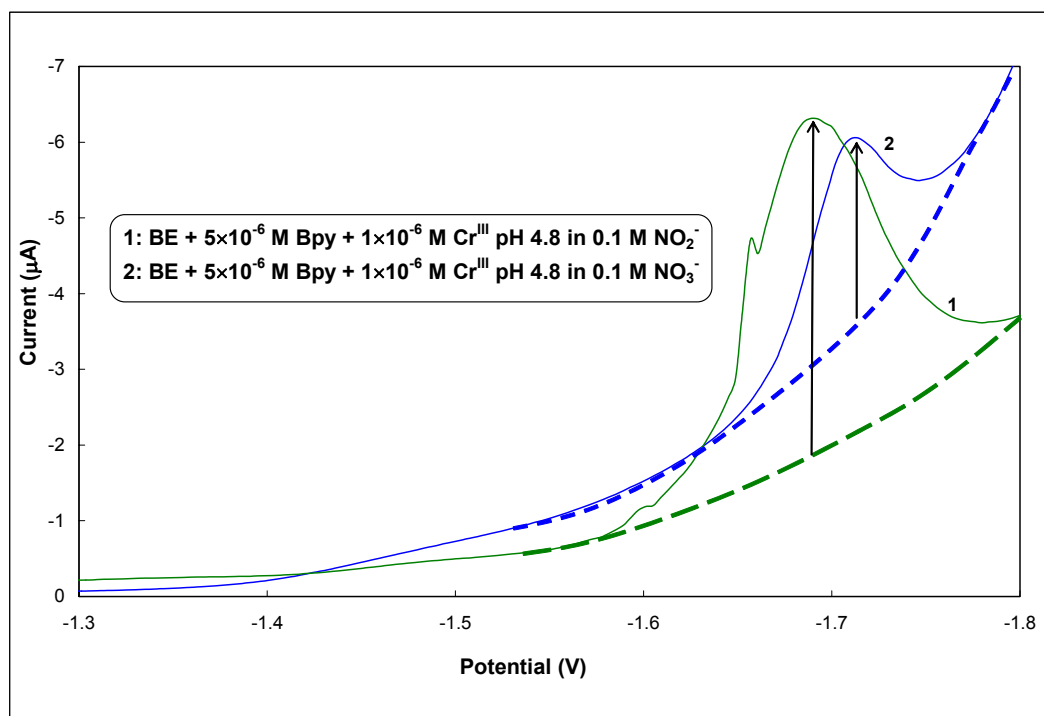


Figure 4.54: DP voltammograms of Cr in the presence of NO_2^- and NO_3^- . Accumulation time 30 s, deposition potential -1 V. HMDE used as working electrode.

Nitrite has been used as catalytic agent in procedures for Cr determination involving Bpy as ligand [84-87]. Elleouet et al [87] reported that nitrate is not involved in the catalytic reaction. In this work nitrate showed evidence to be involved in the catalytic reaction at the electrode (Figures 4.55-4.56). At pH 4.8, the catalytic reduction of hydrogen on Cr showed

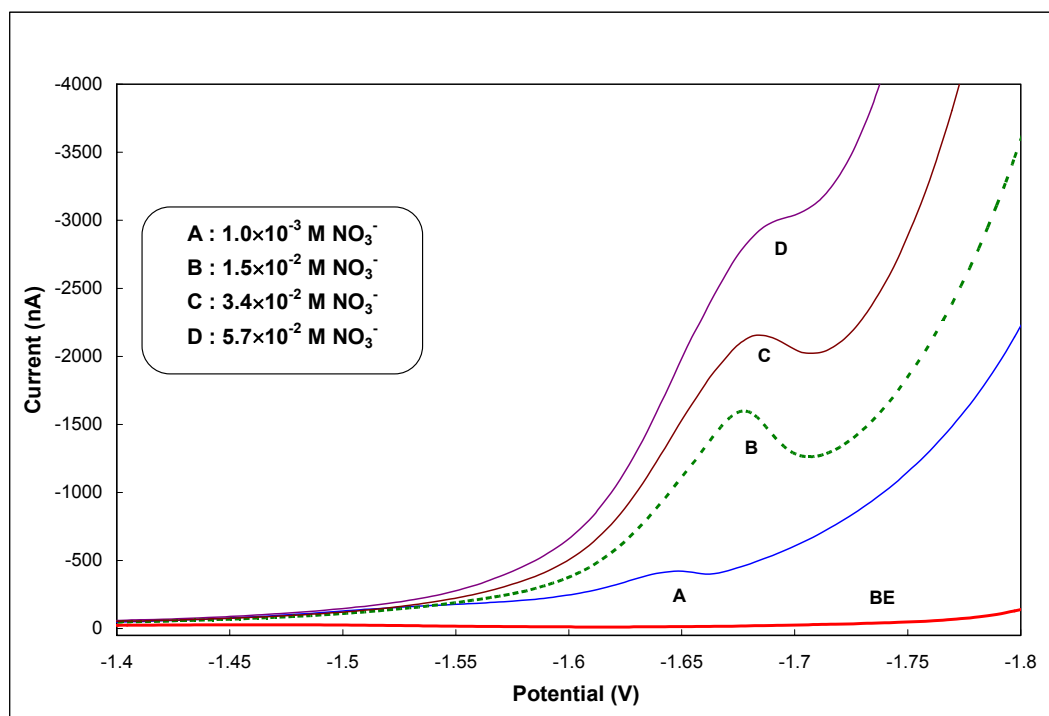


Figure 4.55: DP voltammograms of $5 \times 10^{-6} \text{ M Byp} + 5 \times 10^{-7} \text{ M Cr}^{\text{III}}$, in 0.1 M sodium perchlorate pH 4.8. $t_d: 30 \text{ s}$, $E_d: -1 \text{ V}$. HMDE used as working electrode.

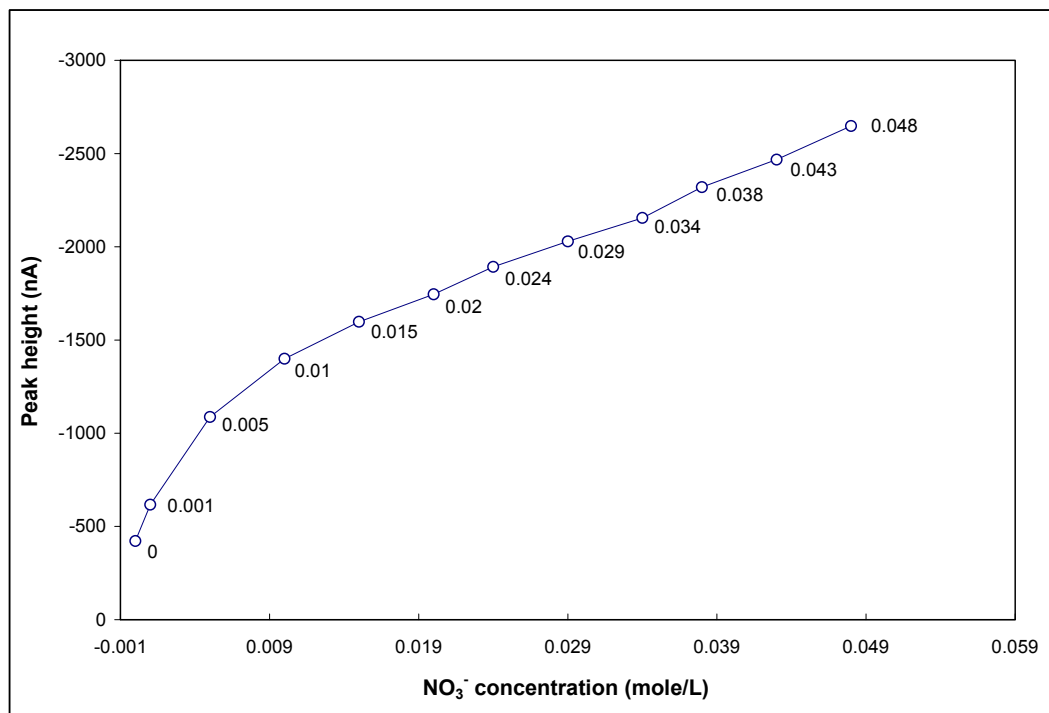


Figure 4.56: Variation of the peak height of $5 \times 10^{-6} \text{ M Byp} + 5 \times 10^{-7} \text{ M Cr}^{\text{III}}$, in 0.1 M sodium perchlorate pH 4.8 as nitrate concentration increases.

an increase in peak height as nitrate concentration was increased. At nitrate concentration higher than 57 mM the reduction peak was overlapped by the hydrogen evolution. The optimum nitrate concentration was selected to be 15 mM, because it gave a reduction peak that was easier to analyse.

Figures 4.57-4.58 recorded at pH 7.5 showed for low nitrate concentration three reduction peaks. Bobrowski and Zarebski [121] reported two reduction peaks at low nitrate concentration ($\approx 10^{-2}$ M) and only one peak at higher nitrate concentration was recorded. In this work one peak was recorded at 4.8×10^{-2} M NO_3^- . The optimum for nitrate concentration was selected as 4.8×10^{-2} M because any further increase of the concentration resulted in the decrease of the peak height.

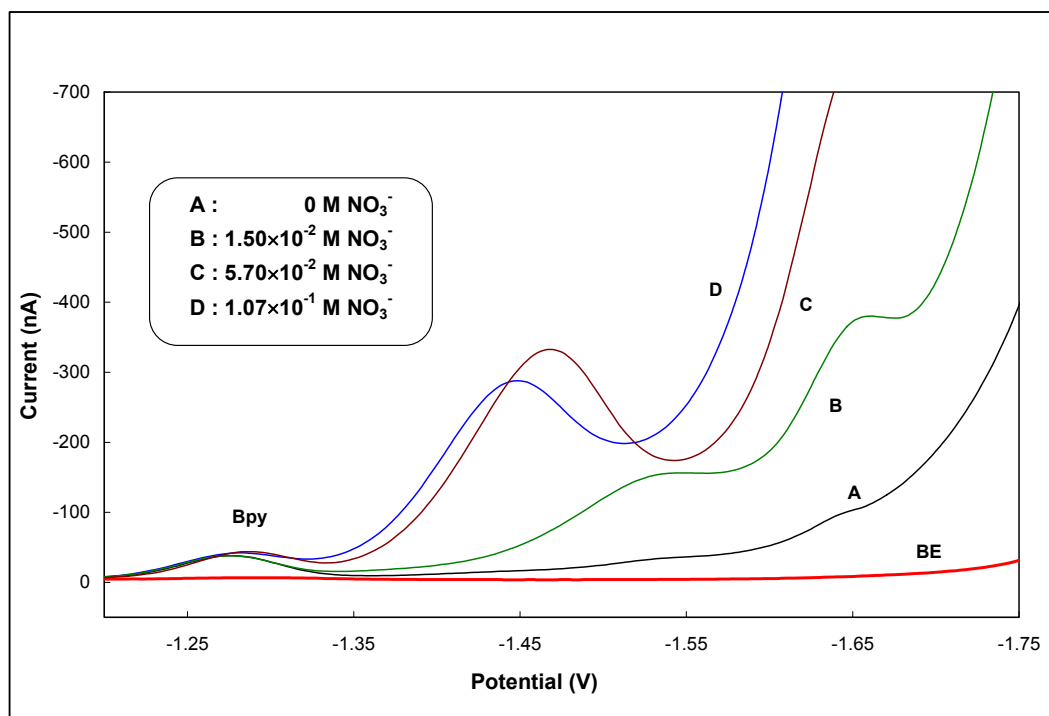


Figure 4.57: DP voltammograms of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium perchlorate pH 7.5. t_d :30 s, E_d :-1 V. HMDE used as working electrode.

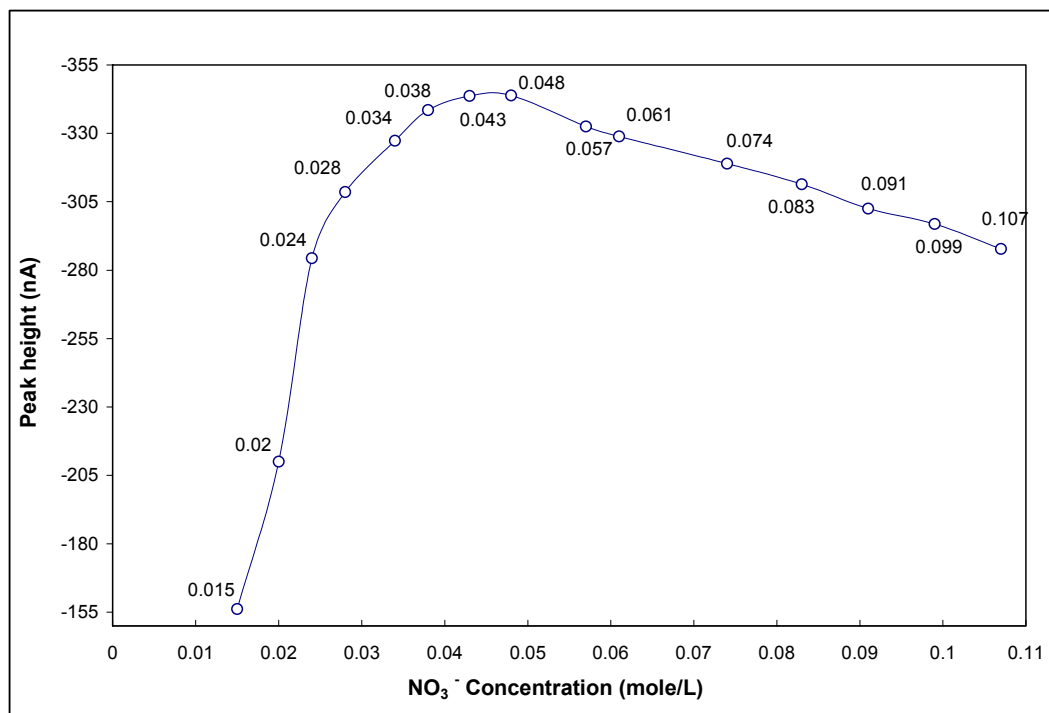


Figure 4.58: Variation of the peak height of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium perchlorate pH 7.5 as nitrate concentration increases.

C. Influence of deposition time on chromium peak height

The deposition time is an important parameter in adsorptive stripping voltammetry. It has a direct impact on the accumulation of the complex at the electrode and the variation of the recorded current. For the reduction peak of Cr^{III} -Bpy recorded at pH 7.5, an increase in the peak height with deposition time was observed up to 20 seconds and then the peak height started to decrease. An optimum deposition time of 20 seconds was selected (Figures 4.59-4.60).

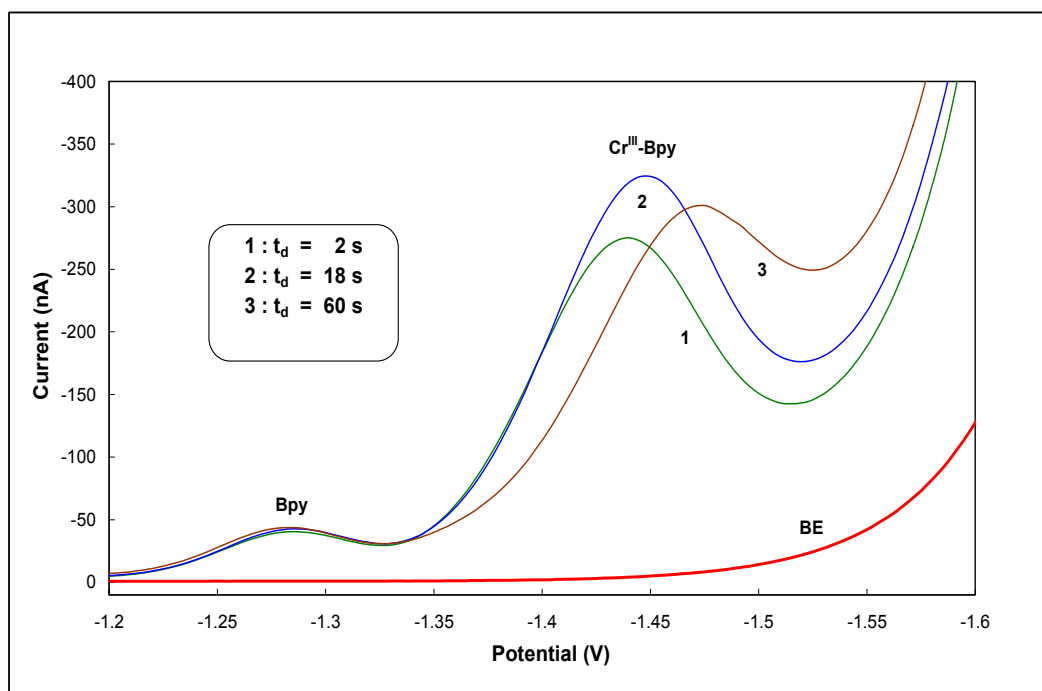


Figure 4.59: DP voltammograms of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 7.5. t_d : X s, E_d : -1 V. HMDE used as working electrode.

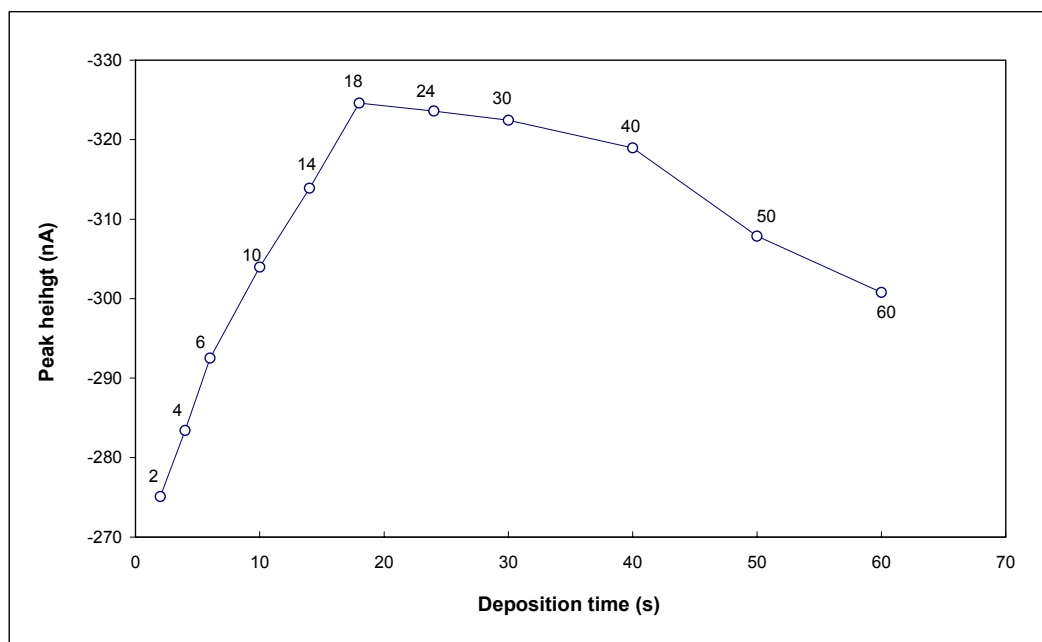


Figure 4.60: Variation of the peak height of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 7.5 as deposition time increases.

In Figures 4.61-4.62, an increase in the peak height with deposition time was observed up to 40 seconds, then the catalytic reduction peak recorded at -1.67 V started to decrease. That decrease of the peak height can be explained as a saturation process occurring onto the electrode surface when the ligand and the complex had been accumulated. An optimum deposition time of 30 seconds was selected.

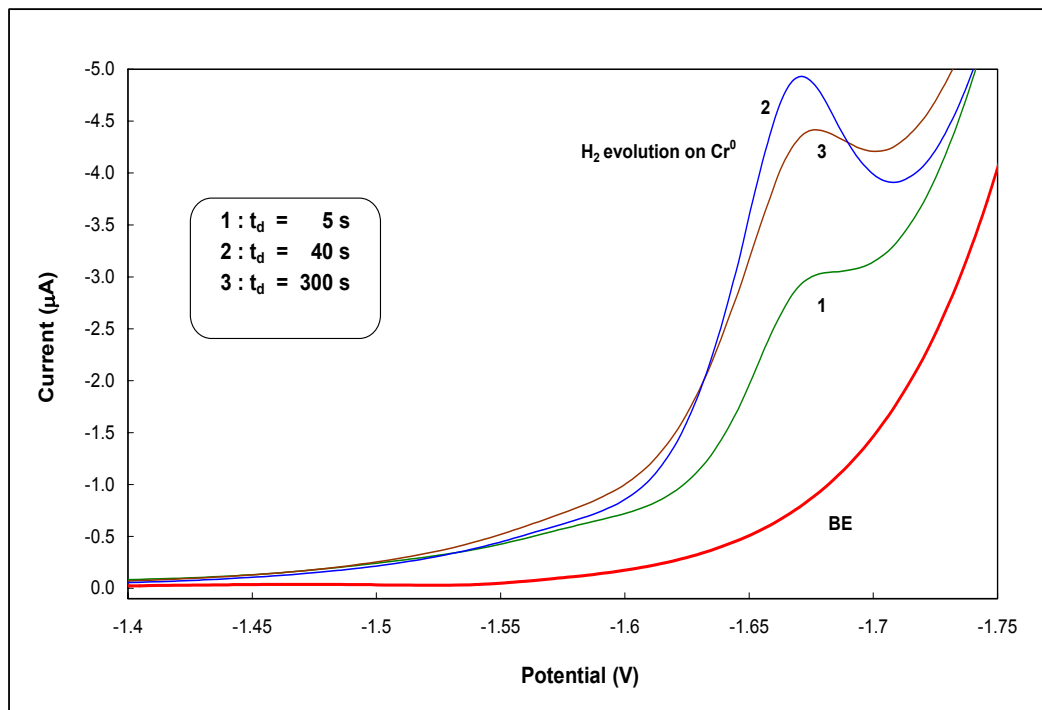


Figure 4.61: DP voltammograms of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 4.8. t_d : X s, E_d : -1 V. HMDE used as working electrode.

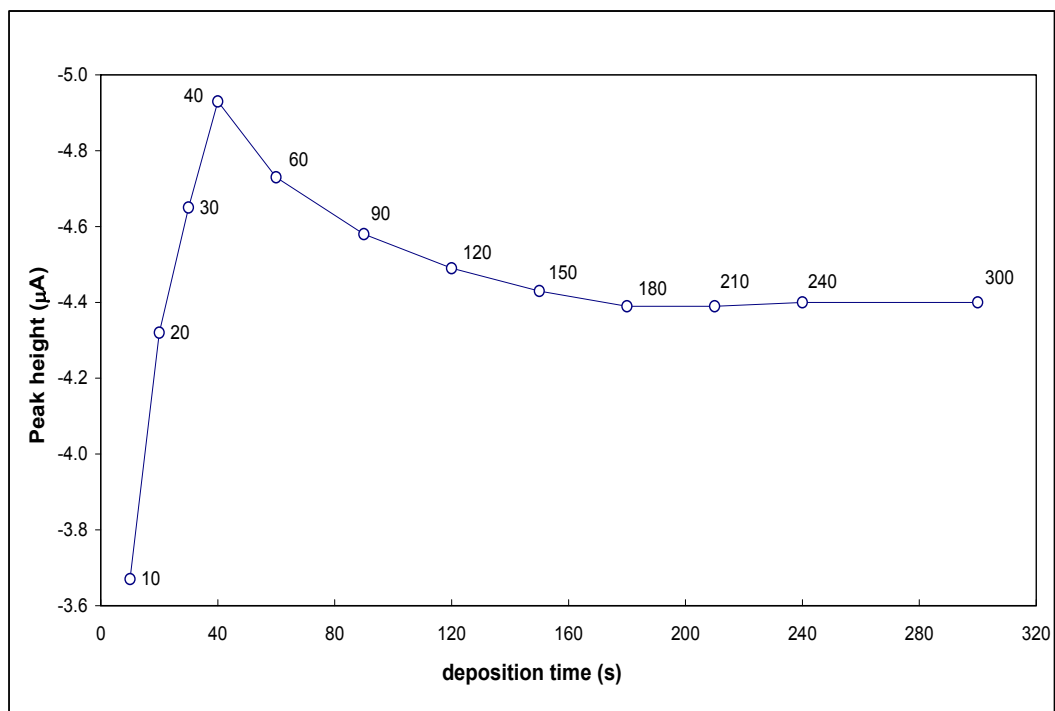


Figure 4.62: Variation of the peak height of 5×10^{-6} M Byp + 5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 4.8 as deposition time increases.

D. Effect of ligand concentration on chromium reduction peak.

No analytical signal could be recorded in the absence of the ligand Bpy. The ligand plays a very important role in the formation of the complex which is adsorbed and then reduced onto the electrode surface. The effect of the ligand on the height of the reduction peak of the complex was investigated by varying the ligand concentration. From Figures 4.63-4.64, at very low ligand concentration (less than $L_T:M_T = \text{ratio } 1$), a high reduction current was recorded. It can also be seen that the shape of the peak was irregular and not smooth. This is due to the low $L_T:M_T$ ratio. At large excess of the ligand concentration ($L_T:M_T = \text{ratio } 12$, voltammogram D in Figure 4.63) a 50 % decrease in the peak height was recorded when compared with voltammogram B for $L_T:M_T = \text{ratio } 1$. This is explained by the ligand activity at the electrode surface (adsorption combined with the reduction of the ligand in competition with the adsorption and reduction of the complex). A related reduction peak of free Bpy could be seen on the voltammogram at -1.3 V. In that particular case an optimum value of 0.3 μM for Bpy concentration was selected. In that case EDTA must be added to prevent the partial consumption of Bpy by other metal

ions present in the sample [84]. Large excess of Bpy must be avoided because it is affecting the analytical signal.

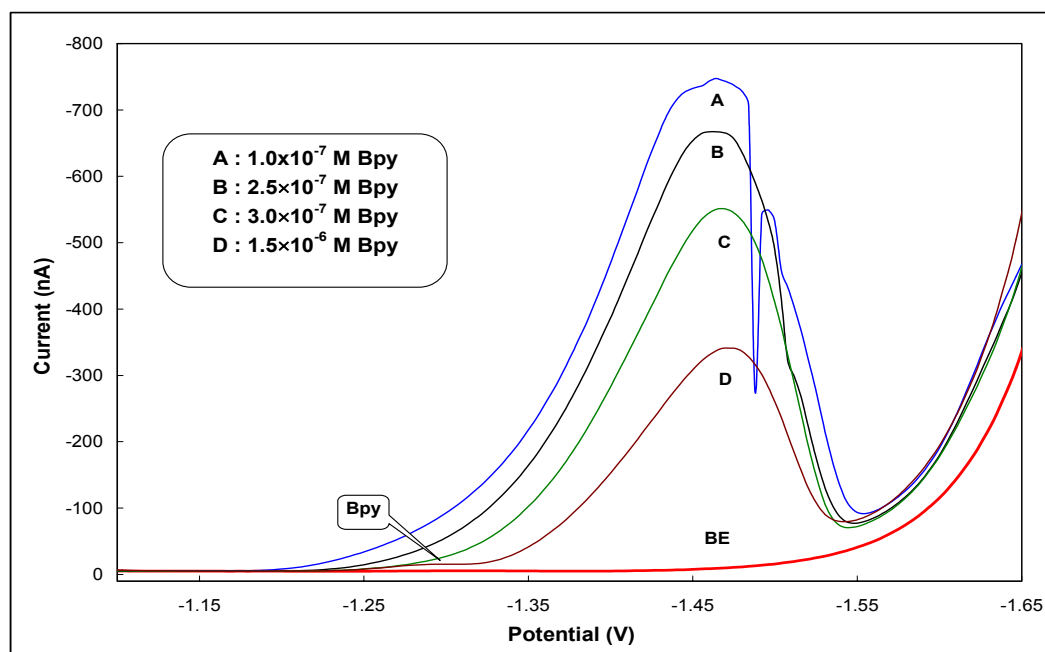


Figure 4.63: Variation of DP voltammograms of 2.5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 7.5 with the increase of Bpy concentration. E_d : -1 V, t_d : 30 s. HMDE used as working electrode.

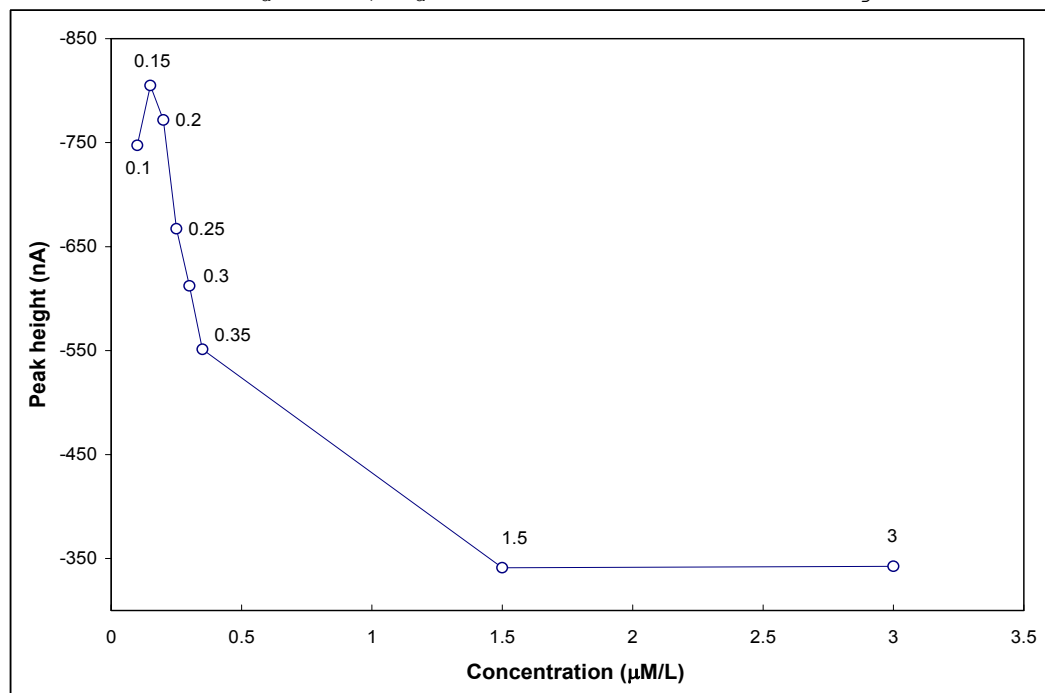


Figure 4.64: Variation of the peak height of 2.5×10^{-7} M Cr^{III} , in 0.1 M sodium nitrate pH 7.5 with the increasing of Bpy concentration.

Chapter 5: Conclusion

The main aim in this work was to understand processes involved in the determination of Cr^{III} by AdCSV using Bpy ligand as a model case. Electroanalytical techniques, GEP and voltammetry (ACV, CV and DPV) were used to investigate the complexation reaction of Cr^{III} with Bpy. The determination of complex stability constants allows the elucidation of the speciation model for Cr^{III} using Bpy.

GEP data were used in the modelling of Cr^{III} -Bpy complexes by the determination of stability constants. The refined model included ML , MLOH , $\text{ML}(\text{OH})_2$ and $\text{ML}(\text{OH})_3$ species and showed the predominance of hydrolyzed complexes. ML_3 complex was totally rejected during the optimization operation. ML_2 complex could be refined and caused a slight change in the relative standard deviation of other species. That might imply the formation of ML_2 species but in a very small quantity. These two last complexes ML_2 and ML_3 require more time to be formed when compared to the others

refined complexes e.g. ML , $MLOH$, $ML(OH)_2$ and $ML(OH)_3$. The results obtained from potentiometry were in good agreement when compared with the voltammetric results.

ACV results showed evidence of adsorption onto the electrode surface of Bpy and Cr^{III} -Bpy complexes but no evidence for Cr^{III} being adsorbed was seen. CV of Bpy and Cr^{III} -Bpy complexes exhibit a Reversible process whereas CV for Cr^{III} exhibits a Quasireversible process. Two kinds of analytical procedures can be developed on basis of two different DP peaks recorded. Interference from Co was stronger when compared with Zn and Ni. Based on voltammetric results three general requirements must be met for chromium determination by AdCSV:

- the ligand or the complex must be adsorbed onto the electrode surface,
- the reaction between the ligand and the metal ion should be fast,
- the stability constant of the complex of interest (the one that is adsorbed and accumulated on the electrode surface) must be larger than that for the competing metal ions (the ligand should be as selective as possible)

The generalized requirements should, in principle, be applicable to any metal-ligand system used in AdCSV. It is assumed that it should lead to an "educated" choice of a suitable ligand in order to increase selectivity and improve the detection limit in ultra trace analysis (ppb-ppt levels) by AdCSV.

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APPENDICES

Appendix 1: Determination of protonation constant 1

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TASK ZBAR BYP 0 PRO1TION
MODL BYP0 H+1
CPLX 0 0 -13800 H 1(-1)
CPLX 1 0 4.750 BY0( 1)H+1( 1)
CONC
VESL IVOL 5.000 ( 0
VESL H+1 ( 89066 0 0
VESL BYP0 1E+05 0 0
BUR1 H+1 -( 2E+05 0 0
ELEC
ZERO H+1 9.88 0
GRAD H+1 8.265 0

```

DATA

0 EMF		PH		ZBAR(H)		POINT		PA		ZBAR(M)		POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID
160.7	4.277	4.29	-0.013	0.61	0.61	0	0.013	0	0	0	0	0	0
159.6	4.296	4.305	-0.01	0.6	0.6	0	0.01	0	0	0	0	0	0
158.5	4.314	4.321	-0.007	0.59	0.59	0	0.007	0	0	0	0	0	0
157.5	4.332	4.337	-0.006	0.58	0.58	0	0.006	0	0	0	0	0	0
156.6	4.347	4.353	-0.006	0.57	0.57	0	0.006	0	0	0	0	0	0
155.6	4.364	4.369	-0.004	0.56	0.56	0	0.004	0	0	0	0	0	0
154.6	4.381	4.384	-0.003	0.55	0.55	0	0.003	0	0	0	0	0	0
153.8	4.395	4.4	-0.005	0.54	0.54	0	0.005	0	0	0	0	0	0
152.8	4.412	4.415	-0.003	0.53	0.53	0	0.003	0	0	0	0	0	0
151.9	4.428	4.431	-0.003	0.53	0.53	0	0.003	0	0	0	0	0	0
151	4.443	4.446	-0.003	0.52	0.52	0	0.003	0	0	0	0	0	0
150.1	4.459	4.461	-0.003	0.51	0.51	0	0.003	0	0	0	0	0	0
149.1	4.476	4.477	-0.001	0.5	0.5	0	0.001	0	0	0	0	0	0
148.2	4.491	4.492	-0.001	0.49	0.49	0	0.001	0	0	0	0	0	0
147.3	4.507	4.508	-0.001	0.48	0.48	0	0.001	0	0	0	0	0	0
146.4	4.522	4.523	-0.001	0.47	0.47	0	0.001	0	0	0	0	0	0
145.5	4.538	4.539	-0.001	0.46	0.46	0	0.001	0	0	0	0	0	0
144.6	4.553	4.554	-0.001	0.45	0.45	0	0.001	0	0	0	0	0	0
143.7	4.568	4.57	-0.001	0.45	0.45	0	0.001	0	0	0	0	0	0
142.8	4.584	4.585	-0.001	0.44	0.44	0	0.001	0	0	0	0	0	0
141.9	4.599	4.601	-0.002	0.43	0.43	0	0.002	0	0	0	0	0	0
140.9	4.616	4.617	0	0.42	0.42	0	0	0	0	0	0	0	0
140	4.632	4.633	-0.001	0.41	0.41	0	0.001	0	0	0	0	0	0
139	4.649	4.649	0	0.4	0.4	0	0	0	0	0	0	0	0
138.1	4.665	4.665	0	0.39	0.39	0	0	0	0	0	0	0	0
137.2	4.68	4.681	-0.001	0.38	0.38	0	0.001	0	0	0	0	0	0
136.2	4.697	4.697	0	0.37	0.37	0	0	0	0	0	0	0	0
135.2	4.714	4.714	0	0.37	0.37	0	0	0	0	0	0	0	0
134.3	4.73	4.731	-0.001	0.36	0.36	0	0.001	0	0	0	0	0	0
133.3	4.747	4.748	-0.001	0.35	0.35	0	0.001	0	0	0	0	0	0
132.3	4.764	4.765	-0.001	0.34	0.34	0	0.001	0	0	0	0	0	0
131.2	4.783	4.782	0.001	0.33	0.33	0	0.001	0	0	0	0	0	0
130.2	4.8	4.8	0	0.32	0.32	0	0	0	0	0	0	0	0
129.1	4.819	4.817	0.002	0.31	0.31	0	0.002	0	0	0	0	0	0
128.1	4.836	4.836	0.001	0.3	0.3	0	0.001	0	0	0	0	0	0
127.1	4.853	4.854	-0.001	0.29	0.29	0	0.001	0	0	0	0	0	0
125.9	4.874	4.873	0.001	0.29	0.29	0	0.001	0	0	0	0	0	0
124.8	4.893	4.892	0.001	0.28	0.28	0	0.001	0	0	0	0	0	0

123.7	4.912	4.911	0	0.27	0.27	0	0	0	0	0	0	0	0	0
122.5	4.932	4.931	0.001	0.26	0.26	0	0.001	0	0	0	0	0	0	0
121.3	4.953	4.952	0.001	0.25	0.25	0	0.001	0	0	0	0	0	0	0
120.1	4.973	4.973	0.001	0.24	0.24	0	0.001	0	0	0	0	0	0	0
118.8	4.996	4.994	0.002	0.23	0.23	0	0.002	0	0	0	0	0	0	0
117.6	5.016	5.016	0.001	0.22	0.22	0	0.001	0	0	0	0	0	0	0
116.2	5.04	5.038	0.002	0.21	0.21	0	0.002	0	0	0	0	0	0	0
114.9	5.063	5.062	0.001	0.21	0.21	0	0.001	0	0	0	0	0	0	0
113.4	5.088	5.086	0.003	0.2	0.2	0	0.003	0	0	0	0	0	0	0
112	5.113	5.111	0.002	0.19	0.19	0	0.002	0	0	0	0	0	0	0
110.5	5.138	5.137	0.002	0.18	0.18	0	0.002	0	0	0	0	0	0	0
108.9	5.166	5.163	0.002	0.17	0.17	0	0.002	0	0	0	0	0	0	0
107.2	5.195	5.191	0.004	0.16	0.16	0	0.004	0	0	0	0	0	0	0
105.6	5.222	5.221	0.002	0.15	0.15	0	0.002	0	0	0	0	0	0	0
103.7	5.255	5.251	0.004	0.14	0.14	0	0.004	0	0	0	0	0	0	0
101.8	5.288	5.284	0.004	0.13	0.13	0	0.004	0	0	0	0	0	0	0
99.9	5.32	5.318	0.002	0.13	0.13	0	0.002	0	0	0	0	0	0	0
97.7	5.358	5.354	0.004	0.12	0.12	0	0.004	0	0	0	0	0	0	0
95.4	5.397	5.393	0.004	0.11	0.11	0	0.004	0	0	0	0	0	0	0
92.9	5.44	5.435	0.005	0.1	0.1	0	0.005	0	0	0	0	0	0	0
90.4	5.483	5.48	0.003	0.09	0.09	0	0.003	0	0	0	0	0	0	0
87.4	5.535	5.53	0.005	0.08	0.08	0	0.005	0	0	0	0	0	0	0
84.3	5.588	5.584	0.003	0.07	0.07	0	0.003	0	0	0	0	0	0	0
80.7	5.65	5.646	0.004	0.06	0.06	0	0.004	0	0	0	0	0	0	0
76.7	5.718	5.716	0.002	0.05	0.05	0	0.002	0	0	0	0	0	0	0
72.1	5.797	5.798	-0.001	0.05	0.05	0	0.001	0	0	0	0	0	0	0
66.5	5.893	5.897	-0.003	0.04	0.04	0	0.003	0	0	0	0	0	0	0
59.7	6.01	6.022	-0.012	0.03	0.03	0	0.012	0	0	0	0	0	0	0

AVERA OF SUI SQUARES

OF	RESIDI	1	2.8E-06	4	5.5E-09	1.3E-05	0	0.0E+00	0	0.0E+00	0.0E+00
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NUMBE OF TITONS = 1

TOTAL MBER INTS = 66

Appendix 2: Determination of protonation constant 2

TASK ZBAR BYP 0 PRO TION
 MODL BYP0 H +1
 CPLX 0 0 -13800 H 1(-1)
 CPLX 1 0 4.790 BY0(1)H +1(1)
 CONC
 VESL IVOL 5.000 (0
 VESL H +1 (89180 0 0
 VESL BYP0 1E+05 0 0
 BUR1 H +1 -(2E+05 0 0
 ELEC
 ZERO H +1 9.88 0
 GRAD H +1 8.265 0

DATA

0 EMF		PH		ZBAR(H)		POINT		PA		ZBAR(M)		POINT		
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID
160.7	4.277	4.288	-0.012	0.61	0.61	0	0.012	0	0	0	0	0	0	0
159.6	4.296	4.304	-0.009	0.6	0.6	0	0.009	0	0	0	0	0	0	0
158.5	4.314	4.32	-0.006	0.59	0.59	0	0.006	0	0	0	0	0	0	0
157.5	4.332	4.336	-0.005	0.58	0.58	0	0.005	0	0	0	0	0	0	0
156.6	4.347	4.352	-0.005	0.57	0.57	0	0.005	0	0	0	0	0	0	0
155.6	4.364	4.368	-0.004	0.56	0.56	0	0.004	0	0	0	0	0	0	0
154.6	4.381	4.383	-0.002	0.55	0.55	0	0.002	0	0	0	0	0	0	0
153.8	4.395	4.399	-0.004	0.55	0.55	0	0.004	0	0	0	0	0	0	0
152.8	4.412	4.415	-0.002	0.54	0.54	0	0.002	0	0	0	0	0	0	0
151.9	4.428	4.43	-0.002	0.53	0.53	0	0.002	0	0	0	0	0	0	0
151	4.443	4.446	-0.002	0.52	0.52	0	0.002	0	0	0	0	0	0	0
150.1	4.459	4.461	-0.002	0.51	0.51	0	0.002	0	0	0	0	0	0	0
149.1	4.476	4.476	-0.001	0.5	0.5	0	0.001	0	0	0	0	0	0	0
148.2	4.491	4.492	-0.001	0.49	0.49	0	0.001	0	0	0	0	0	0	0
147.3	4.507	4.507	-0.001	0.48	0.48	0	0.001	0	0	0	0	0	0	0
146.4	4.522	4.523	-0.001	0.47	0.47	0	0.001	0	0	0	0	0	0	0
145.5	4.538	4.538	-0.001	0.47	0.47	0	0.001	0	0	0	0	0	0	0
144.6	4.553	4.554	-0.001	0.46	0.46	0	0.001	0	0	0	0	0	0	0
143.7	4.568	4.57	-0.001	0.45	0.45	0	0.001	0	0	0	0	0	0	0
142.8	4.584	4.585	-0.001	0.44	0.44	0	0.001	0	0	0	0	0	0	0
141.9	4.599	4.601	-0.002	0.43	0.43	0	0.002	0	0	0	0	0	0	0
140.9	4.616	4.617	0	0.42	0.42	0	0	0	0	0	0	0	0	0
140	4.632	4.633	-0.001	0.41	0.41	0	0.001	0	0	0	0	0	0	0
139	4.649	4.649	0	0.4	0.4	0	0	0	0	0	0	0	0	0
138.1	4.665	4.665	0	0.39	0.39	0	0	0	0	0	0	0	0	0
137.2	4.68	4.681	-0.001	0.39	0.39	0	0.001	0	0	0	0	0	0	0
136.2	4.697	4.698	0	0.38	0.38	0	0	0	0	0	0	0	0	0
135.2	4.714	4.714	0	0.37	0.37	0	0	0	0	0	0	0	0	0
134.3	4.73	4.731	-0.001	0.36	0.36	0	0.001	0	0	0	0	0	0	0
133.3	4.747	4.748	-0.001	0.35	0.35	0	0.001	0	0	0	0	0	0	0
132.3	4.764	4.765	-0.001	0.34	0.34	0	0.001	0	0	0	0	0	0	0
131.2	4.783	4.782	0.001	0.33	0.33	0	0.001	0	0	0	0	0	0	0
130.2	4.8	4.8	0	0.32	0.32	0	0	0	0	0	0	0	0	0
129.1	4.819	4.818	0.001	0.31	0.31	0	0.001	0	0	0	0	0	0	0
128.1	4.836	4.836	0	0.31	0.31	0	0	0	0	0	0	0	0	0
127.1	4.853	4.854	-0.001	0.3	0.3	0	0.001	0	0	0	0	0	0	0
125.9	4.874	4.873	0.001	0.29	0.29	0	0.001	0	0	0	0	0	0	0
124.8	4.893	4.892	0.001	0.28	0.28	0	0.001	0	0	0	0	0	0	0

123.7	4.912	4.912	0	0.27	0.27	0	0	0	0	0	0	0	0	0
122.5	4.932	4.932	0.001	0.26	0.26	0	0.001	0	0	0	0	0	0	0
121.3	4.953	4.952	0.001	0.25	0.25	0	0.001	0	0	0	0	0	0	0
120.1	4.973	4.973	0.001	0.24	0.24	0	0.001	0	0	0	0	0	0	0
118.8	4.996	4.994	0.002	0.23	0.23	0	0.002	0	0	0	0	0	0	0
117.6	5.016	5.016	0	0.23	0.23	0	0	0	0	0	0	0	0	0
116.2	5.04	5.039	0.002	0.22	0.22	0	0.002	0	0	0	0	0	0	0
114.9	5.063	5.062	0.001	0.21	0.21	0	0.001	0	0	0	0	0	0	0
113.4	5.088	5.086	0.003	0.2	0.2	0	0.003	0	0	0	0	0	0	0
112	5.113	5.111	0.002	0.19	0.19	0	0.002	0	0	0	0	0	0	0
110.5	5.138	5.136	0.002	0.18	0.18	0	0.002	0	0	0	0	0	0	0
108.9	5.166	5.163	0.003	0.17	0.17	0	0.003	0	0	0	0	0	0	0
107.2	5.195	5.191	0.004	0.16	0.16	0	0.004	0	0	0	0	0	0	0
105.6	5.222	5.22	0.002	0.15	0.15	0	0.002	0	0	0	0	0	0	0
103.7	5.255	5.251	0.004	0.14	0.14	0	0.004	0	0	0	0	0	0	0
101.8	5.288	5.283	0.005	0.14	0.14	0	0.005	0	0	0	0	0	0	0
99.9	5.32	5.317	0.003	0.13	0.13	0	0.003	0	0	0	0	0	0	0
97.7	5.358	5.353	0.005	0.12	0.12	0	0.005	0	0	0	0	0	0	0
95.4	5.397	5.392	0.006	0.11	0.11	0	0.006	0	0	0	0	0	0	0
92.9	5.44	5.433	0.007	0.1	0.1	0	0.007	0	0	0	0	0	0	0
90.4	5.483	5.478	0.005	0.09	0.09	0	0.005	0	0	0	0	0	0	0
87.4	5.535	5.527	0.007	0.08	0.08	0	0.007	0	0	0	0	0	0	0
84.3	5.588	5.582	0.006	0.07	0.07	0	0.006	0	0	0	0	0	0	0
80.7	5.65	5.643	0.007	0.06	0.06	0	0.007	0	0	0	0	0	0	0
76.7	5.718	5.712	0.007	0.06	0.06	0	0.007	0	0	0	0	0	0	0
72.1	5.797	5.792	0.005	0.05	0.05	0	0.005	0	0	0	0	0	0	0
66.5	5.893	5.89	0.004	0.04	0.04	0	0.004	0	0	0	0	0	0	0
59.7	6.01	6.012	-0.002	0.03	0.03	0	0.002	0	0	0	0	0	0	0
50.6	6.166	6.18	-0.014	0.02	0.02	0	0.014	0	0	0	0	0	0	0

AVERAF SUM QUARES

OF	RESIDI	1	5.0E-06	3	6.1E-11	1.5E-05	0	0.0E+00	0	0.0E+00	0.0E+00
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NUMBEF TITRONS = 1

TOTAL BER OINTS = 67

Appendix 3: Determination of protonation constant 3

TASK ZBAR BYP 0 PROTONATION

MODL BYP0 H+1

CPLX 0 0 -13 800 H+1(-1)

CPLX 1 0 4.930 BY0(1) H+1(1)

CONC

VESL IVOL 0.000 (0

VESL H+1 0 90951 0 0

VESL BYP0 1E+05 0 0

BUR1 H+1 -C 2E+05 0 0

ELEC

ZERO H+1 4.18 0

GRAD H+1 8.056 0

DATA

0 EMF		PH		ZBAR(H)			POINT		PA			ZBAR(M)		POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID	
155.7	4.28	4.256	0.024	0.63	0.63	0	0.024	0	0	0	0	0	0	0	
155.2	4.289	4.268	0.02	0.63	0.63	0	0.02	0	0	0	0	0	0	0	
154.6	4.299	4.281	0.018	0.62	0.62	0	0.018	0	0	0	0	0	0	0	
154	4.309	4.293	0.017	0.61	0.61	0	0.017	0	0	0	0	0	0	0	
153.3	4.321	4.305	0.017	0.61	0.61	0	0.017	0	0	0	0	0	0	0	
152.8	4.33	4.317	0.013	0.6	0.6	0	0.013	0	0	0	0	0	0	0	
152.2	4.34	4.329	0.012	0.59	0.59	0	0.012	0	0	0	0	0	0	0	
151.7	4.349	4.341	0.008	0.59	0.59	0	0.008	0	0	0	0	0	0	0	
151	4.361	4.352	0.009	0.58	0.58	0	0.009	0	0	0	0	0	0	0	
150.4	4.371	4.364	0.007	0.57	0.57	0	0.007	0	0	0	0	0	0	0	
149.9	4.38	4.376	0.004	0.57	0.57	0	0.004	0	0	0	0	0	0	0	
149.3	4.39	4.387	0.003	0.56	0.56	0	0.003	0	0	0	0	0	0	0	
148.7	4.401	4.399	0.002	0.55	0.55	0	0.002	0	0	0	0	0	0	0	
148.1	4.411	4.411	0	0.55	0.55	0	0	0	0	0	0	0	0	0	
147.5	4.421	4.422	-0.001	0.54	0.54	0	0.001	0	0	0	0	0	0	0	
146.9	4.432	4.434	-0.002	0.53	0.53	0	0.002	0	0	0	0	0	0	0	
146.3	4.442	4.445	-0.003	0.53	0.53	0	0.003	0	0	0	0	0	0	0	
145.7	4.452	4.457	-0.005	0.52	0.52	0	0.005	0	0	0	0	0	0	0	
145.1	4.463	4.468	-0.006	0.51	0.51	0	0.006	0	0	0	0	0	0	0	
144.5	4.473	4.48	-0.007	0.51	0.51	0	0.007	0	0	0	0	0	0	0	
143.9	4.483	4.491	-0.008	0.5	0.5	0	0.008	0	0	0	0	0	0	0	
143.4	4.492	4.503	-0.011	0.49	0.49	0	0.011	0	0	0	0	0	0	0	
142.7	4.504	4.514	-0.01	0.49	0.49	0	0.01	0	0	0	0	0	0	0	
142.1	4.514	4.526	-0.012	0.48	0.48	0	0.012	0	0	0	0	0	0	0	
141.5	4.525	4.537	-0.013	0.47	0.47	0	0.013	0	0	0	0	0	0	0	
140.9	4.535	4.549	-0.014	0.47	0.47	0	0.014	0	0	0	0	0	0	0	
140.3	4.545	4.561	-0.015	0.46	0.46	0	0.015	0	0	0	0	0	0	0	
139.7	4.556	4.572	-0.016	0.45	0.45	0	0.016	0	0	0	0	0	0	0	
139.1	4.566	4.584	-0.018	0.45	0.45	0	0.018	0	0	0	0	0	0	0	
138.5	4.576	4.595	-0.019	0.44	0.44	0	0.019	0	0	0	0	0	0	0	
137.8	4.588	4.607	-0.019	0.43	0.43	0	0.019	0	0	0	0	0	0	0	
137.2	4.599	4.619	-0.02	0.43	0.43	0	0.02	0	0	0	0	0	0	0	
136.6	4.609	4.631	-0.022	0.42	0.42	0	0.022	0	0	0	0	0	0	0	
135.9	4.621	4.642	-0.021	0.41	0.41	0	0.021	0	0	0	0	0	0	0	
135.3	4.631	4.654	-0.023	0.41	0.41	0	0.023	0	0	0	0	0	0	0	
134.6	4.643	4.666	-0.023	0.4	0.4	0	0.023	0	0	0	0	0	0	0	
134	4.654	4.678	-0.025	0.39	0.39	0	0.025	0	0	0	0	0	0	0	
133.3	4.666	4.69	-0.025	0.39	0.39	0	0.025	0	0	0	0	0	0	0	

132.6	4.678	4.703	-0.025	0.38	0.38	0	0.025	0	0	0	0	0	0	0
131.9	4.69	4.715	-0.025	0.37	0.38	0	0.025	0	0	0	0	0	0	0
131.3	4.7	4.727	-0.027	0.37	0.37	0	0.027	0	0	0	0	0	0	0
130.6	4.712	4.74	-0.027	0.36	0.36	0	0.027	0	0	0	0	0	0	0
129.9	4.724	4.752	-0.028	0.36	0.36	0	0.028	0	0	0	0	0	0	0
129.2	4.736	4.765	-0.028	0.35	0.35	0	0.028	0	0	0	0	0	0	0
128.5	4.749	4.778	-0.029	0.34	0.34	0	0.029	0	0	0	0	0	0	0
126.6	4.781	4.79	-0.009	0.34	0.34	0	0.009	0	0	0	0	0	0	0
124.9	4.811	4.803	0.007	0.33	0.33	0	0.007	0	0	0	0	0	0	0
123.7	4.831	4.817	0.015	0.32	0.32	0	0.015	0	0	0	0	0	0	0
122.7	4.848	4.83	0.019	0.32	0.32	0	0.019	0	0	0	0	0	0	0
121.8	4.864	4.843	0.021	0.31	0.31	0	0.021	0	0	0	0	0	0	0
121	4.878	4.857	0.021	0.3	0.3	0	0.021	0	0	0	0	0	0	0
120.2	4.891	4.871	0.021	0.3	0.3	0	0.021	0	0	0	0	0	0	0
119.4	4.905	4.885	0.021	0.29	0.29	0	0.021	0	0	0	0	0	0	0
118.6	4.919	4.899	0.02	0.28	0.28	0	0.02	0	0	0	0	0	0	0
117.9	4.931	4.913	0.018	0.28	0.28	0	0.018	0	0	0	0	0	0	0
117.1	4.945	4.928	0.017	0.27	0.27	0	0.017	0	0	0	0	0	0	0
116.3	4.959	4.942	0.016	0.26	0.26	0	0.016	0	0	0	0	0	0	0
115.4	4.974	4.957	0.017	0.26	0.26	0	0.017	0	0	0	0	0	0	0
114.6	4.988	4.973	0.015	0.25	0.25	0	0.015	0	0	0	0	0	0	0
113.8	5.002	4.988	0.013	0.24	0.24	0	0.013	0	0	0	0	0	0	0
112.9	5.017	5.004	0.013	0.24	0.24	0	0.013	0	0	0	0	0	0	0
112	5.033	5.02	0.012	0.23	0.23	0	0.012	0	0	0	0	0	0	0
111.1	5.048	5.037	0.011	0.22	0.22	0	0.011	0	0	0	0	0	0	0
110.2	5.064	5.054	0.01	0.22	0.22	0	0.01	0	0	0	0	0	0	0
109.2	5.081	5.071	0.01	0.21	0.21	0	0.01	0	0	0	0	0	0	0
108.2	5.098	5.089	0.01	0.2	0.2	0	0.01	0	0	0	0	0	0	0
107.2	5.115	5.107	0.009	0.2	0.2	0	0.009	0	0	0	0	0	0	0
106.2	5.133	5.125	0.007	0.19	0.19	0	0.007	0	0	0	0	0	0	0
105.1	5.152	5.144	0.007	0.18	0.18	0	0.007	0	0	0	0	0	0	0
104	5.171	5.164	0.006	0.18	0.18	0	0.006	0	0	0	0	0	0	0
102.9	5.189	5.184	0.005	0.17	0.17	0	0.005	0	0	0	0	0	0	0
101.7	5.21	5.205	0.005	0.16	0.16	0	0.005	0	0	0	0	0	0	0
100.5	5.231	5.227	0.004	0.16	0.16	0	0.004	0	0	0	0	0	0	0
99.2	5.253	5.249	0.004	0.15	0.15	0	0.004	0	0	0	0	0	0	0
97.9	5.276	5.272	0.003	0.14	0.14	0	0.003	0	0	0	0	0	0	0
96.5	5.3	5.296	0.003	0.14	0.14	0	0.003	0	0	0	0	0	0	0
95.1	5.324	5.321	0.002	0.13	0.13	0	0.002	0	0	0	0	0	0	0
93.6	5.35	5.348	0.002	0.12	0.12	0	0.002	0	0	0	0	0	0	0
92	5.377	5.375	0.002	0.12	0.12	0	0.002	0	0	0	0	0	0	0
90.3	5.407	5.404	0.002	0.11	0.11	0	0.002	0	0	0	0	0	0	0
88.5	5.438	5.435	0.003	0.1	0.1	0	0.003	0	0	0	0	0	0	0
86.6	5.47	5.467	0.003	0.1	0.1	0	0.003	0	0	0	0	0	0	0
84.7	5.503	5.501	0.002	0.09	0.09	0	0.002	0	0	0	0	0	0	0
82.5	5.541	5.538	0.003	0.08	0.08	0	0.003	0	0	0	0	0	0	0
80.2	5.58	5.577	0.003	0.08	0.08	0	0.003	0	0	0	0	0	0	0
77.7	5.624	5.62	0.003	0.07	0.07	0	0.003	0	0	0	0	0	0	0
75	5.67	5.667	0.003	0.06	0.06	0	0.003	0	0	0	0	0	0	0
72	5.722	5.719	0.003	0.06	0.06	0	0.003	0	0	0	0	0	0	0
68.6	5.78	5.777	0.004	0.05	0.05	0	0.004	0	0	0	0	0	0	0
64.8	5.846	5.842	0.003	0.04	0.04	0	0.003	0	0	0	0	0	0	0
60.5	5.92	5.919	0.001	0.04	0.04	0	0.001	0	0	0	0	0	0	0
55.2	6.011	6.01	0.001	0.03	0.03	0	0.001	0	0	0	0	0	0	0
48.8	6.121	6.124	-0.003	0.02	0.02	0	0.003	0	0	0	0	0	0	0
40.6	6.263	6.276	-0.014	0.02	0.02	0	0.014	0	0	0	0	0	0	0

AVERAGE OF SUM SQUARES

OF RESIDUAL	2	5.0E-06	4	1.8E-08	2.1E-04	0	0.0E+00	0	0.0E+00	0.0E+00
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NUMBER OF TITRATIONS = 1

TOTAL MEASUREMENTS = 94

Appendix 4: Determination of Cr^{III}-Bpy stability constants (+CrOH) L_T:M_T ratio 1

TASK ZBAR 'BYP 0 COMFES WIT Cr(III) ratio 1 bis

MODL Cr+3 BYP0 H 1

CPLX 0 0 -13.800 H+1(-1)

CPLX 0 0 4.920 BY0(1) H+1(1)

CPLX 0 0 -4.000 Cr 3(1) H+1(-1)

CPLX 1 0 -2.780 Cr 3(1) B' P0(1) H+1(- 1)

CPLX 1 0 -7.870 Cr 3(1) B' P0(1) H+1(- 2)

CPLX 1 0 -12.100 Cr 3(1) B' P0(1) H+1(- 3)

CONC

VESL IVOL 0.000 (0

VESL H+1 (1E+05 0 0

VESL Cr+3 (49990 0 0

VESL BYP0 50579 0 0

BUR1 H+1 -(2E+05 0 0

ELEC

ZERO H+1 5.51 0

GRAD H+1 8.987 0

DATA

0 EMF		PH		ZBAR(H)			POINT		PA			ZBAR(M)			POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID		
253.8	2.572	2.589	-0.017	0.93	0.95	-0.024	0.029	4.317	4.289	0.028	0.06	0.04	0.025	0.037		
251.9	2.604	2.622	-0.018	0.92	0.95	-0.023	0.029	4.29	4.262	0.029	0.07	0.04	0.024	0.038		
250	2.636	2.657	-0.021	0.92	0.94	-0.025	0.032	4.265	4.233	0.032	0.07	0.04	0.026	0.042		
247.8	2.674	2.694	-0.02	0.91	0.94	-0.023	0.03	4.232	4.202	0.031	0.07	0.05	0.024	0.039		
245.6	2.711	2.732	-0.021	0.91	0.93	-0.022	0.031	4.201	4.169	0.032	0.08	0.05	0.024	0.04		
243.2	2.752	2.773	-0.022	0.9	0.93	-0.021	0.03	4.166	4.135	0.031	0.08	0.06	0.022	0.038		
240.8	2.792	2.816	-0.024	0.9	0.92	-0.021	0.032	4.133	4.099	0.034	0.09	0.06	0.023	0.041		
238.1	2.838	2.862	-0.024	0.89	0.91	-0.019	0.031	4.094	4.061	0.033	0.09	0.07	0.021	0.039		
235.2	2.887	2.91	-0.023	0.88	0.9	-0.016	0.028	4.052	4.021	0.031	0.1	0.08	0.018	0.036		
232.1	2.94	2.961	-0.021	0.87	0.89	-0.013	0.025	4.007	3.979	0.028	0.1	0.09	0.015	0.032		
228.9	2.994	3.014	-0.02	0.86	0.87	-0.011	0.023	3.962	3.937	0.025	0.11	0.1	0.013	0.028		
225.4	3.053	3.069	-0.015	0.85	0.86	-0.008	0.017	3.912	3.893	0.019	0.12	0.11	0.009	0.021		
221.7	3.116	3.125	-0.009	0.84	0.84	-0.004	0.01	3.86	3.849	0.011	0.13	0.13	0.005	0.012		
217.9	3.181	3.183	-0.002	0.82	0.82	-0.001	0.002	3.808	3.806	0.003	0.14	0.14	0.001	0.003		
214	3.247	3.241	0.006	0.8	0.8	0.002	0.006	3.756	3.763	-0.007	0.16	0.16	-0.003	0.007		
210.1	3.313	3.299	0.014	0.78	0.77	0.004	0.015	3.706	3.723	-0.016	0.18	0.18	-0.006	0.018		
206.3	3.377	3.356	0.022	0.75	0.74	0.006	0.022	3.66	3.685	-0.025	0.2	0.2	-0.009	0.026		
202.7	3.438	3.411	0.027	0.72	0.71	0.006	0.028	3.62	3.65	-0.031	0.22	0.23	-0.011	0.032		
199.3	3.496	3.466	0.03	0.69	0.68	0.006	0.031	3.585	3.619	-0.034	0.25	0.26	-0.012	0.036		
196	3.552	3.518	0.034	0.66	0.65	0.006	0.034	3.553	3.591	-0.038	0.27	0.29	-0.013	0.04		
193	3.603	3.569	0.034	0.62	0.61	0.006	0.035	3.53	3.568	-0.038	0.3	0.32	-0.012	0.04		
190.3	3.648	3.617	0.031	0.58	0.58	0.005	0.031	3.514	3.548	-0.035	0.34	0.35	-0.011	0.036		
187.7	3.693	3.664	0.028	0.55	0.54	0.004	0.028	3.501	3.532	-0.031	0.37	0.38	-0.01	0.033		
185.3	3.733	3.71	0.023	0.51	0.5	0.003	0.023	3.495	3.521	-0.026	0.41	0.42	-0.008	0.027		
183	3.772	3.754	0.018	0.47	0.47	0.002	0.018	3.494	3.514	-0.02	0.45	0.45	-0.006	0.021		
180.8	3.809	3.797	0.013	0.43	0.43	0.001	0.013	3.498	3.512	-0.014	0.49	0.49	-0.004	0.015		
178.7	3.845	3.838	0.007	0.39	0.39	0.001	0.007	3.508	3.515	-0.008	0.53	0.53	-0.002	0.008		
176.5	3.882	3.879	0.004	0.35	0.35	0	0.004	3.52	3.525	-0.004	0.57	0.57	-0.001	0.004		
174.4	3.918	3.918	0	0.31	0.31	0	0	3.541	3.541	0	0.62	0.62	0	0		
172.3	3.954	3.957	-0.003	0.27	0.27	0	0.003	3.569	3.566	0.003	0.66	0.66	0.001	0.004		
170.2	3.989	3.995	-0.005	0.23	0.23	0	0.005	3.608	3.601	0.006	0.71	0.71	0.001	0.006		
168.2	4.023	4.032	-0.009	0.19	0.19	-0.001	0.009	3.662	3.652	0.01	0.76	0.76	0.002	0.01		
166.1	4.059	4.069	-0.01	0.15	0.15	-0.001	0.01	3.737	3.725	0.012	0.81	0.81	0.002	0.012		

163.9	4.096	4.105	-0.009	0.11	0.11	-0.001	0.009	3.845	3.834	0.011	0.86	0.86	0.002	0.011
161.9	4.13	4.141	-0.011	0.06	0.06	-0.001	0.011	4.03	4.014	0.015	0.92	0.92	0.002	0.015
159.7	4.167	4.177	-0.01	0.02	0.02	0	0.01	4.442	4.424	0.018	0.98	0.98	0.001	0.018
157.6	4.203	4.213	-0.01	-0.02	-0.02	0	0.01	0	0	0	0	0	0	0
155.5	4.238	4.248	-0.01	-0.06	-0.06	0	0.01	0	0	0	0	0	0	0
153.3	4.276	4.283	-0.008	-0.1	-0.1	0	0.008	0	0	0	0	0	0	0
151.2	4.311	4.319	-0.007	-0.14	-0.14	0	0.007	0	0	0	0	0	0	0
149.1	4.347	4.354	-0.007	-0.19	-0.19	0	0.007	0	0	0	0	0	0	0
146.9	4.384	4.389	-0.005	-0.23	-0.23	0	0.005	0	0	0	0	0	0	0
144.9	4.418	4.425	-0.006	-0.27	-0.27	0	0.006	0	0	0	0	0	0	0
142.7	4.455	4.46	-0.004	-0.31	-0.31	0	0.004	0	0	0	0	0	0	0
140.7	4.489	4.495	-0.006	-0.35	-0.35	0	0.006	0	0	0	0	0	0	0
138.5	4.527	4.531	-0.004	-0.4	-0.4	0	0.004	0	0	0	0	0	0	0
136.3	4.564	4.566	-0.002	-0.44	-0.44	0	0.002	0	0	0	0	0	0	0
134.3	4.598	4.602	-0.004	-0.48	-0.48	0	0.004	0	0	0	0	0	0	0
132.1	4.635	4.637	-0.002	-0.52	-0.52	0	0.002	0	0	0	0	0	0	0
129.9	4.672	4.672	0	-0.56	-0.56	0	0	0	0	0	0	0	0	0
127.8	4.708	4.707	0.001	-0.61	-0.61	0	0.001	0	0	0	0	0	0	0
125.6	4.745	4.742	0.003	-0.65	-0.65	0	0.003	0	0	0	0	0	0	0
123.5	4.781	4.776	0.005	-0.69	-0.69	0	0.005	0	0	0	0	0	0	0
121.4	4.816	4.81	0.006	-0.73	-0.73	0	0.006	0	0	0	0	0	0	0
119.4	4.85	4.843	0.007	-0.78	-0.78	0	0.007	0	0	0	0	0	0	0
117.3	4.886	4.876	0.01	-0.82	-0.82	0	0.01	0	0	0	0	0	0	0
115.2	4.922	4.908	0.013	-0.86	-0.86	0	0.013	0	0	0	0	0	0	0
113.2	4.955	4.94	0.016	-0.91	-0.91	0	0.016	0	0	0	0	0	0	0
111.2	4.989	4.97	0.019	-0.95	-0.95	0	0.019	0	0	0	0	0	0	0
110.4	5.003	5	0.003	-0.99	-0.99	0	0.003	0	0	0	0	0	0	0
109.6	5.017	5.03	-0.013	-1.03	-1.03	0	0.013	0	0	0	0	0	0	0
109.2	5.023	5.058	-0.035	-1.08	-1.08	0	0.035	0	0	0	0	0	0	0

AVERAGE SUM SQUARES

OF RESIDUALS 2 6.1E-05 7 8.9E-06 3.4E-04 5 8.7E-05 1 7.7E-03 7.6E-04

NUMBER OF TITRATIONS = 1

TOTAL NUMBER OF POINTS = 62

Appendix 5: Determination of Cr^{III}-Bpy stability constants (+CrOH) L_T:M_T ratio 2

TASK ZBAR 1 BYP 0 COMIES WITCr(III) ratio 2 bis

MODL Cr+3 BYP0 1

CPLX C0 -13.7 800 H 1(-1)

CPLX C0 4.4 920 BY0(1) H+1(1)

CPLX C0 -4.0 000 Cr 3(1) H+1(-1)

CPLX 10 1.3 500 Cr 3(1) B P0(1)

CPLX 10 -2.1 850 Cr 3(1) B P0(1) H+1(- 1)

CPLX 10 -7.7 240 Cr 3(1) B P0(1) H+1(- 2)

CPLX 10 -12.6 800 Cr 3(1) B P0(1) H+1(- 3)

CONC

VESL I VOL 5.000 (0

VESL I+1 0.0 1E+05 0 0

VESL Cr+3 0.1 33452 0 0

VESL EYP0 0 67439 0 0

BUR1 I 1 2E+05 0 0

ELEC

ZERO I+1 40 4.56 0

GRAD I+1 5 8.972 0

DATA

0 EMF		PH		ZBAR(I H)				POINT		PA		ZBAR(I M)				POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	OBS
247.6	2.662	2.667	-0.005	0.96	0.96	-0.004	0.007	4.054	4.046	0.007	0.06	0.05	0.009	0.012			
245.8	2.692	2.694	-0.002	0.96	0.96	-0.002	0.003	4.026	4.023	0.003	0.05	0.05	0.004	0.005			
244.2	2.719	2.723	-0.004	0.95	0.96	-0.003	0.005	4.003	3.998	0.005	0.06	0.05	0.006	0.008			
242.4	2.75	2.753	-0.003	0.95	0.95	-0.002	0.004	3.976	3.972	0.004	0.06	0.06	0.004	0.006			
240.5	2.782	2.784	-0.002	0.95	0.95	-0.001	0.002	3.947	3.945	0.002	0.06	0.06	0.002	0.003			
238.7	2.813	2.816	-0.003	0.95	0.95	-0.002	0.004	3.922	3.917	0.004	0.07	0.07	0.004	0.006			
236.6	2.848	2.85	-0.002	0.94	0.94	-0.001	0.002	3.89	3.888	0.002	0.07	0.07	0.002	0.003			
234.4	2.885	2.885	0.001	0.94	0.94	0	0.001	3.857	3.858	-0.001	0.08	0.08	-0.001	0.001			
232.4	2.919	2.921	-0.002	0.93	0.93	-0.001	0.002	3.828	3.826	0.002	0.09	0.08	0.002	0.003			
230.2	2.957	2.959	-0.002	0.93	0.93	-0.001	0.003	3.796	3.793	0.003	0.09	0.09	0.002	0.004			
227.6	3.001	2.998	0.002	0.92	0.92	0.001	0.003	3.757	3.76	-0.003	0.1	0.1	-0.002	0.004			
225	3.045	3.039	0.006	0.92	0.91	0.002	0.006	3.718	3.725	-0.007	0.1	0.11	-0.005	0.009			
222.6	3.086	3.081	0.005	0.91	0.91	0.002	0.005	3.684	3.69	-0.006	0.11	0.12	-0.004	0.007			
220.3	3.125	3.123	0.001	0.9	0.9	0	0.002	3.652	3.654	-0.002	0.13	0.13	-0.001	0.002			
217.8	3.167	3.166	0.001	0.89	0.89	0	0.001	3.617	3.618	-0.001	0.14	0.14	-0.001	0.001			
215.1	3.213	3.21	0.003	0.88	0.88	0.001	0.003	3.579	3.582	-0.003	0.15	0.16	-0.002	0.004			
212.5	3.257	3.253	0.003	0.87	0.86	0.001	0.003	3.543	3.547	-0.004	0.17	0.17	-0.002	0.004			
210	3.299	3.297	0.002	0.85	0.85	0	0.002	3.51	3.512	-0.002	0.19	0.19	-0.002	0.003			
207.6	3.34	3.34	0	0.84	0.84	0	0	3.479	3.479	0	0.21	0.21	0	0			
205	3.384	3.382	0.002	0.82	0.82	0	0.002	3.444	3.446	-0.002	0.22	0.22	-0.001	0.002			
202.5	3.426	3.424	0.002	0.81	0.81	0	0.002	3.412	3.415	-0.003	0.24	0.24	-0.002	0.003			
200.3	3.464	3.465	-0.001	0.79	0.79	0	0.001	3.386	3.385	0.001	0.27	0.27	0.001	0.001			
197.9	3.504	3.504	0	0.78	0.78	0	0	3.357	3.357	0	0.29	0.29	0	0			
195.6	3.543	3.543	0.001	0.76	0.76	0	0.001	3.33	3.331	-0.001	0.31	0.31	-0.001	0.001			
193.4	3.581	3.58	0.001	0.74	0.74	0	0.001	3.305	3.306	-0.001	0.33	0.33	-0.001	0.001			
191.3	3.616	3.616	0	0.73	0.73	0	0	3.282	3.282	0	0.36	0.36	0	0			
189.3	3.65	3.652	-0.001	0.71	0.71	0	0.001	3.262	3.26	0.001	0.39	0.39	0.001	0.002			
187.2	3.686	3.686	0	0.69	0.69	0	0	3.24	3.24	0	0.41	0.41	0	0			
185.3	3.718	3.719	-0.001	0.67	0.67	0	0.001	3.222	3.221	0.001	0.44	0.44	0.001	0.002			
183.3	3.752	3.752	0	0.65	0.65	0	0	3.203	3.203	0	0.47	0.47	0	0			
181.6	3.781	3.783	-0.003	0.63	0.63	0	0.003	3.189	3.187	0.003	0.5	0.49	0.002	0.003			
179.7	3.813	3.814	-0.001	0.61	0.61	0	0.001	3.173	3.172	0.001	0.52	0.52	0.001	0.002			

178.1	3.84	3.845	-0.004	0.59	0.59	0	0.004	3.162	3.158	0.005	0.56	0.55	0.003	0.006
176.3	3.871	3.874	-0.003	0.57	0.57	0	0.003	3.149	3.145	0.004	0.59	0.58	0.003	0.004
174.6	3.899	3.903	-0.004	0.55	0.55	0	0.004	3.138	3.134	0.004	0.62	0.62	0.003	0.005
172.9	3.928	3.931	-0.003	0.53	0.53	0	0.003	3.127	3.124	0.003	0.65	0.65	0.003	0.004
171.2	3.957	3.959	-0.002	0.51	0.51	0	0.002	3.117	3.115	0.002	0.68	0.68	0.002	0.003
169.6	3.984	3.987	-0.003	0.49	0.49	0	0.003	3.11	3.107	0.003	0.72	0.71	0.002	0.004
168	4.011	4.014	-0.003	0.47	0.47	0	0.003	3.103	3.101	0.003	0.75	0.75	0.002	0.003
166.4	4.039	4.041	-0.002	0.45	0.45	0	0.002	3.097	3.095	0.002	0.79	0.78	0.002	0.003
164.8	4.066	4.067	-0.001	0.43	0.43	0	0.001	3.093	3.091	0.001	0.82	0.82	0.001	0.002
163.2	4.093	4.093	0	0.41	0.41	0	0	3.089	3.088	0	0.86	0.86	0	0.001
161.7	4.118	4.119	-0.001	0.39	0.39	0	0.001	3.088	3.087	0.001	0.9	0.9	0.001	0.001
160.1	4.145	4.145	0.001	0.37	0.37	0	0.001	3.087	3.087	-0.001	0.94	0.94	-0.001	0.001
158.6	4.171	4.17	0.001	0.35	0.35	0	0.001	3.088	3.089	-0.001	0.98	0.98	-0.001	0.001
157.1	4.196	4.195	0.001	0.33	0.33	0	0.001	3.092	3.093	-0.001	1.02	1.02	-0.001	0.001
155.5	4.223	4.221	0.003	0.31	0.31	0	0.003	3.095	3.098	-0.003	1.06	1.07	-0.002	0.004
154.1	4.247	4.246	0.001	0.29	0.29	0	0.001	3.104	3.106	-0.002	1.11	1.11	-0.001	0.002
152.6	4.273	4.271	0.002	0.26	0.26	0	0.002	3.114	3.116	-0.002	1.16	1.16	-0.002	0.003
151.1	4.298	4.296	0.002	0.24	0.24	0	0.002	3.126	3.129	-0.003	1.21	1.21	-0.002	0.003
149.6	4.323	4.321	0.003	0.22	0.22	0	0.003	3.142	3.145	-0.003	1.26	1.26	-0.002	0.004
148.1	4.349	4.345	0.003	0.2	0.2	0	0.003	3.161	3.165	-0.004	1.32	1.32	-0.003	0.004
146.7	4.373	4.37	0.002	0.18	0.18	0	0.002	3.187	3.189	-0.002	1.37	1.38	-0.002	0.003
145.1	4.4	4.396	0.004	0.16	0.16	0	0.004	3.215	3.22	-0.004	1.43	1.44	-0.003	0.005
143.7	4.423	4.421	0.003	0.14	0.14	0	0.003	3.255	3.258	-0.003	1.5	1.5	-0.002	0.003
142.2	4.449	4.446	0.003	0.12	0.12	0	0.003	3.303	3.306	-0.003	1.56	1.56	-0.002	0.004
140.7	4.474	4.471	0.003	0.1	0.1	0	0.003	3.365	3.368	-0.003	1.63	1.63	-0.001	0.004
139.2	4.5	4.497	0.003	0.08	0.08	0	0.003	3.448	3.451	-0.003	1.71	1.71	-0.001	0.003
137.7	4.525	4.523	0.003	0.05	0.05	0	0.003	3.566	3.569	-0.003	1.79	1.79	-0.001	0.003
136.2	4.551	4.549	0.002	0.03	0.03	0	0.002	3.755	3.758	-0.002	1.87	1.87	0	0.003
134.7	4.576	4.575	0.001	0.01	0.01	0	0.001	4.164	4.166	-0.002	1.96	1.96	0	0.002
133.2	4.602	4.601	0	-0.01	-0.01	0	0	0	0	0	0	0	0	0
131.6	4.629	4.628	0.001	-0.03	-0.03	0	0.001	0	0	0	0	0	0	0
130	4.656	4.655	0.001	-0.05	-0.05	0	0.001	0	0	0	0	0	0	0
128.5	4.681	4.682	-0.001	-0.07	-0.07	0	0.001	0	0	0	0	0	0	0
126.9	4.708	4.709	-0.001	-0.09	-0.09	0	0.001	0	0	0	0	0	0	0
125.3	4.735	4.737	-0.002	-0.11	-0.11	0	0.002	0	0	0	0	0	0	0
123.7	4.763	4.765	-0.003	-0.14	-0.14	0	0.003	0	0	0	0	0	0	0
122.1	4.79	4.794	-0.004	-0.16	-0.16	0	0.004	0	0	0	0	0	0	0
120.4	4.819	4.822	-0.004	-0.18	-0.18	0	0.004	0	0	0	0	0	0	0
118.7	4.847	4.851	-0.004	-0.2	-0.2	0	0.004	0	0	0	0	0	0	0
117.1	4.875	4.88	-0.005	-0.22	-0.22	0	0.005	0	0	0	0	0	0	0
115.3	4.905	4.909	-0.004	-0.24	-0.24	0	0.004	0	0	0	0	0	0	0
113.6	4.934	4.938	-0.004	-0.26	-0.26	0	0.004	0	0	0	0	0	0	0
111.9	4.963	4.967	-0.004	-0.28	-0.28	0	0.004	0	0	0	0	0	0	0
110.2	4.992	4.996	-0.004	-0.31	-0.31	0	0.004	0	0	0	0	0	0	0
108.5	5.02	5.024	-0.004	-0.33	-0.33	0	0.004	0	0	0	0	0	0	0
106.7	5.051	5.053	-0.002	-0.35	-0.35	0	0.002	0	0	0	0	0	0	0
104.9	5.081	5.081	0	-0.37	-0.37	0	0	0	0	0	0	0	0	0
103.2	5.11	5.109	0.002	-0.39	-0.39	0	0.002	0	0	0	0	0	0	0
101.4	5.141	5.136	0.005	-0.41	-0.41	0	0.005	0	0	0	0	0	0	0
99.7	5.17	5.162	0.007	-0.43	-0.43	0	0.007	0	0	0	0	0	0	0
98.1	5.197	5.188	0.008	-0.46	-0.46	0	0.008	0	0	0	0	0	0	0
96.5	5.224	5.214	0.01	-0.48	-0.48	0	0.01	0	0	0	0	0	0	0
94.8	5.253	5.239	0.014	-0.5	-0.5	0	0.014	0	0	0	0	0	0	0
93.3	5.278	5.264	0.015	-0.52	-0.52	0	0.015	0	0	0	0	0	0	0
92.8	5.287	5.287	-0.001	-0.54	-0.54	0	0.001	0	0	0	0	0	0	0
91.8	5.304	5.311	-0.007	-0.56	-0.56	0	0.007	0	0	0	0	0	0	0

91.6 5.307 5.334 -0.027 -0.58 -0.58 0 0.027 0 0 0 0 0 0 0

AVERAGE SUM OF SQUARES

OF RESIDUALS 2 2.2E-06 5 7.2E-08 2.3E-05 8 3.5E-07 6 0.0E+00 1.4E-05

NUMBER OF TITRATIONS = 1

TOTAL NUMBER OF POINTS = 89

Appendix 6: Determination of Cr^{III}-Bpy stability constants (+CrOH) L_T:M_T ratio 3

TASK ZBAR 'BYP 0 COMFES WIT Cr(III) ratio 3 bis

MODL Cr+3 BYP0 H 1

CPLX 0 0 -13 800 H+1(-1)

CPLX 0 0 4.920 BY0(1) H+1(1)

CPLX 0 0 -4.000 Cr-3(1) H+1(-1)

CPLX 1 0 1.460 Cr-3(1) B'P0(1)

CPLX 1 0 -1.060 Cr-3(1) B'P0(1) H+1(- 1)

CPLX 1 0 -7.010 Cr-3(1) B'P0(1) H+1(- 2)

CPLX 1 0 -12 300 Cr-3(1) B'P0(1) H+1(- 3)

CONC

VESL IVOL 0.000 (0

VESL H+1 (1E+05 0 0

VESL Cr+3 (23167 0 0

VESL BYP0 76685 0 0

BUR1 H+1 -(2E+05 0 0

ELEC

ZERO H+1 4.26 0

GRAD H+1 8.859 0

DATA

0 EMF		PH		ZBAR(H)			POINT		PA			ZBAR(M)			POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID		
263.9	2.385	2.385	0	0.98	0.98	0	0	4.229	4.229	0	0.02	0.03	0	0		
263.1	2.398	2.398	0	0.98	0.98	0	0.001	4.218	4.218	-0.001	0.02	0.03	-0.001	0.001		
262.3	2.412	2.412	0	0.98	0.98	0	0	4.207	4.207	0	0.03	0.03	-0.001	0.001		
261.6	2.424	2.425	-0.002	0.98	0.98	-0.002	0.003	4.198	4.196	0.003	0.03	0.03	0.007	0.007		
260.8	2.437	2.44	-0.002	0.98	0.98	-0.003	0.003	4.187	4.184	0.003	0.04	0.03	0.009	0.009		
259.9	2.453	2.454	-0.002	0.98	0.98	-0.002	0.002	4.174	4.172	0.002	0.04	0.03	0.006	0.006		
259	2.468	2.469	-0.001	0.98	0.98	-0.001	0.002	4.161	4.159	0.002	0.03	0.03	0.004	0.004		
258.2	2.482	2.484	-0.003	0.98	0.98	-0.003	0.004	4.15	4.146	0.004	0.04	0.03	0.009	0.01		
257.2	2.499	2.5	-0.001	0.98	0.98	-0.001	0.002	4.135	4.133	0.002	0.04	0.03	0.004	0.004		
256.3	2.514	2.516	-0.002	0.98	0.98	-0.002	0.002	4.122	4.12	0.003	0.04	0.03	0.006	0.006		
255.4	2.529	2.532	-0.003	0.98	0.98	-0.003	0.004	4.11	4.106	0.004	0.04	0.04	0.009	0.01		
254.4	2.546	2.549	-0.003	0.98	0.98	-0.002	0.003	4.095	4.092	0.004	0.04	0.04	0.008	0.008		
253.4	2.563	2.566	-0.003	0.97	0.98	-0.002	0.004	4.081	4.077	0.004	0.05	0.04	0.008	0.009		
252.4	2.58	2.583	-0.003	0.97	0.98	-0.003	0.004	4.066	4.062	0.004	0.05	0.04	0.009	0.01		
251.3	2.599	2.601	-0.003	0.97	0.97	-0.002	0.003	4.05	4.046	0.004	0.05	0.04	0.007	0.008		
250.3	2.616	2.62	-0.004	0.97	0.97	-0.003	0.005	4.036	4.03	0.006	0.05	0.04	0.012	0.013		
249.1	2.636	2.639	-0.003	0.97	0.97	-0.002	0.004	4.018	4.014	0.004	0.05	0.05	0.008	0.009		
248	2.655	2.659	-0.004	0.97	0.97	-0.003	0.005	4.002	3.996	0.005	0.06	0.05	0.01	0.012		
246.8	2.675	2.679	-0.004	0.97	0.97	-0.003	0.005	3.984	3.979	0.005	0.06	0.05	0.01	0.011		
245.6	2.696	2.7	-0.005	0.97	0.97	-0.003	0.006	3.966	3.96	0.006	0.06	0.05	0.011	0.012		
244.3	2.718	2.722	-0.004	0.96	0.97	-0.003	0.005	3.947	3.941	0.005	0.06	0.05	0.009	0.011		
243	2.74	2.744	-0.004	0.96	0.97	-0.003	0.005	3.927	3.922	0.006	0.07	0.06	0.009	0.011		
241.7	2.762	2.767	-0.005	0.96	0.96	-0.003	0.006	3.908	3.901	0.007	0.07	0.06	0.011	0.013		
240.2	2.787	2.791	-0.004	0.96	0.96	-0.002	0.004	3.885	3.88	0.005	0.07	0.06	0.007	0.009		
238.8	2.811	2.816	-0.005	0.96	0.96	-0.002	0.005	3.864	3.859	0.006	0.08	0.07	0.009	0.01		
237.2	2.838	2.841	-0.003	0.96	0.96	-0.001	0.003	3.84	3.836	0.004	0.08	0.07	0.005	0.006		
235.7	2.864	2.868	-0.004	0.95	0.95	-0.002	0.004	3.818	3.813	0.005	0.08	0.08	0.007	0.008		
234	2.893	2.895	-0.002	0.95	0.95	-0.001	0.002	3.792	3.789	0.003	0.08	0.08	0.003	0.004		
232.3	2.922	2.923	-0.001	0.95	0.95	-0.001	0.001	3.766	3.764	0.002	0.09	0.09	0.002	0.003		
230.6	2.95	2.952	-0.001	0.94	0.94	-0.001	0.002	3.74	3.739	0.002	0.09	0.09	0.002	0.003		
228.8	2.981	2.982	-0.001	0.94	0.94	0	0.001	3.713	3.713	0.001	0.1	0.1	0.001	0.001		
226.9	3.013	3.012	0.001	0.94	0.94	0	0.001	3.685	3.686	-0.001	0.1	0.11	-0.001	0.002		

225.1	3.044	3.044	0	0.93	0.93	0	0	3.658	3.658	0	0.11	0.11	0	0
223.1	3.078	3.076	0.002	0.93	0.93	0.001	0.002	3.628	3.63	-0.002	0.12	0.12	-0.002	0.003
221.2	3.11	3.109	0.001	0.92	0.92	0	0.001	3.6	3.602	-0.001	0.13	0.13	-0.001	0.002
219.1	3.146	3.142	0.004	0.92	0.92	0.001	0.004	3.569	3.573	-0.004	0.14	0.14	-0.004	0.006
217.1	3.18	3.176	0.004	0.91	0.91	0.001	0.004	3.54	3.544	-0.004	0.15	0.15	-0.004	0.006
215	3.215	3.21	0.005	0.9	0.9	0.001	0.006	3.509	3.515	-0.006	0.16	0.16	-0.006	0.009
213	3.249	3.244	0.005	0.9	0.9	0.001	0.005	3.481	3.486	-0.006	0.17	0.18	-0.006	0.008
211	3.283	3.278	0.005	0.89	0.89	0.001	0.005	3.452	3.458	-0.006	0.19	0.19	-0.006	0.008
208.9	3.319	3.312	0.007	0.88	0.88	0.001	0.007	3.422	3.43	-0.008	0.2	0.21	-0.008	0.011
206.9	3.353	3.346	0.008	0.87	0.87	0.001	0.008	3.395	3.403	-0.008	0.21	0.22	-0.008	0.011
205	3.385	3.379	0.007	0.86	0.86	0.001	0.007	3.369	3.376	-0.007	0.23	0.24	-0.007	0.01
203.1	3.418	3.411	0.006	0.85	0.85	0.001	0.006	3.343	3.35	-0.007	0.25	0.26	-0.007	0.01
201.2	3.45	3.443	0.007	0.84	0.84	0.001	0.007	3.318	3.325	-0.007	0.27	0.27	-0.007	0.01
199.4	3.481	3.475	0.006	0.83	0.83	0.001	0.006	3.295	3.301	-0.006	0.29	0.29	-0.006	0.009
197.7	3.509	3.505	0.004	0.82	0.82	0	0.004	3.273	3.278	-0.004	0.31	0.31	-0.004	0.006
195.9	3.54	3.535	0.005	0.81	0.81	0.001	0.005	3.25	3.255	-0.005	0.33	0.33	-0.005	0.007
194.2	3.569	3.564	0.004	0.8	0.8	0	0.004	3.229	3.234	-0.005	0.35	0.35	-0.005	0.007
192.7	3.594	3.593	0.001	0.79	0.79	0	0.001	3.212	3.214	-0.002	0.37	0.38	-0.002	0.002
191.1	3.622	3.621	0.001	0.78	0.78	0	0.001	3.193	3.194	-0.001	0.4	0.4	-0.001	0.001
189.6	3.647	3.648	-0.001	0.76	0.76	0	0.001	3.176	3.175	0.001	0.42	0.42	0.001	0.001
188.1	3.673	3.674	-0.002	0.75	0.75	0	0.002	3.159	3.158	0.002	0.45	0.45	0.002	0.003
186.6	3.698	3.7	-0.002	0.74	0.74	0	0.002	3.143	3.141	0.002	0.47	0.47	0.003	0.004
185.2	3.722	3.726	-0.004	0.73	0.73	0	0.004	3.128	3.124	0.004	0.5	0.49	0.005	0.006
183.7	3.747	3.775	-0.003	0.71	0.71	0	0.003	3.112	3.109	0.003	0.52	0.52	0.004	0.005
182.4	3.769	3.774	-0.005	0.7	0.7	0	0.005	3.099	3.094	0.005	0.55	0.54	0.007	0.008
181	3.793	3.798	-0.005	0.69	0.69	0	0.005	3.085	3.08	0.005	0.58	0.57	0.007	0.008
179.7	3.815	3.821	-0.006	0.68	0.68	0	0.006	3.073	3.067	0.006	0.6	0.6	0.008	0.01
178.4	3.837	3.844	-0.007	0.66	0.66	0	0.007	3.061	3.054	0.007	0.63	0.62	0.009	0.012
177.1	3.859	3.867	-0.007	0.65	0.65	0	0.007	3.049	3.042	0.007	0.66	0.65	0.01	0.012
175.8	3.881	3.889	-0.007	0.64	0.64	0	0.007	3.038	3.031	0.007	0.69	0.68	0.01	0.012
174.5	3.904	3.91	-0.007	0.62	0.62	0	0.007	3.026	3.02	0.007	0.72	0.71	0.01	0.012
173.2	3.926	3.931	-0.006	0.61	0.61	0	0.006	3.015	3.009	0.006	0.74	0.74	0.009	0.01
172	3.946	3.952	-0.006	0.6	0.6	0	0.006	3.006	3	0.007	0.77	0.76	0.01	0.012
170.7	3.968	3.973	-0.005	0.58	0.58	0	0.005	2.996	2.99	0.005	0.8	0.79	0.008	0.009
169.5	3.989	3.994	-0.005	0.57	0.57	0	0.005	2.987	2.982	0.005	0.83	0.82	0.008	0.01
168.3	4.009	4.014	-0.005	0.56	0.56	0	0.005	2.978	2.973	0.005	0.86	0.85	0.008	0.009
167.1	4.029	4.034	-0.004	0.54	0.54	0	0.004	2.97	2.966	0.005	0.89	0.89	0.007	0.009
165.9	4.05	4.054	-0.004	0.53	0.53	0	0.004	2.962	2.958	0.004	0.92	0.92	0.006	0.007
164.7	4.07	4.073	-0.003	0.52	0.52	0	0.003	2.955	2.952	0.003	0.96	0.95	0.005	0.006
163.5	4.09	4.093	-0.002	0.5	0.5	0	0.002	2.948	2.946	0.002	0.99	0.98	0.003	0.004
162.4	4.109	4.112	-0.003	0.49	0.49	0	0.003	2.942	2.94	0.003	1.02	1.02	0.004	0.005
161.2	4.13	4.131	-0.001	0.48	0.48	0	0.001	2.936	2.935	0.001	1.05	1.05	0.002	0.003
160	4.15	4.15	0	0.46	0.46	0	0	2.93	2.93	0	1.09	1.09	0	0
159	4.167	4.169	-0.002	0.45	0.45	0	0.002	2.927	2.926	0.002	1.13	1.12	0.003	0.004
157.8	4.187	4.187	0	0.43	0.43	0	0	2.922	2.922	0	1.16	1.16	0	0
156.7	4.206	4.206	0	0.42	0.42	0	0	2.919	2.919	0	1.2	1.2	0	0
155.5	4.226	4.225	0.002	0.41	0.41	0	0.002	2.914	2.916	-0.002	1.23	1.24	-0.003	0.004
154.5	4.243	4.243	0	0.39	0.39	0	0	2.914	2.914	0	1.27	1.27	0	0
153.3	4.264	4.262	0.002	0.38	0.38	0	0.002	2.911	2.913	-0.002	1.31	1.32	-0.004	0.004
152.2	4.282	4.28	0.002	0.37	0.37	0	0.002	2.909	2.912	-0.002	1.35	1.36	-0.004	0.005
151.1	4.301	4.298	0.003	0.35	0.35	0	0.003	2.909	2.912	-0.003	1.39	1.4	-0.005	0.006
150	4.32	4.317	0.003	0.34	0.34	0	0.003	2.909	2.912	-0.003	1.44	1.44	-0.005	0.006
148.9	4.339	4.335	0.003	0.32	0.32	0	0.003	2.91	2.914	-0.003	1.48	1.49	-0.006	0.007
147.9	4.355	4.354	0.002	0.31	0.31	0	0.002	2.914	2.916	-0.002	1.53	1.54	-0.003	0.004
146.7	4.376	4.372	0.004	0.3	0.3	0	0.004	2.915	2.919	-0.004	1.58	1.58	-0.007	0.008
145.7	4.393	4.39	0.002	0.28	0.28	0	0.002	2.92	2.923	-0.002	1.63	1.63	-0.004	0.005

144.5	4.413	4.409	0.004	0.27	0.27	0	0.004	2.923	2.927	-0.004	1.68	1.69	-0.008	0.009
143.5	4.43	4.427	0.003	0.25	0.25	0	0.003	2.931	2.933	-0.003	1.73	1.74	-0.005	0.006
142.4	4.449	4.446	0.003	0.24	0.24	0	0.003	2.938	2.941	-0.003	1.79	1.8	-0.005	0.006
141.3	4.468	4.465	0.003	0.23	0.23	0	0.003	2.946	2.949	-0.003	1.85	1.85	-0.005	0.006
140.2	4.486	4.483	0.003	0.21	0.21	0	0.003	2.957	2.96	-0.003	1.91	1.91	-0.005	0.006
139	4.507	4.502	0.005	0.2	0.2	0	0.005	2.967	2.972	-0.005	1.97	1.98	-0.008	0.009
137.9	4.525	4.521	0.004	0.19	0.19	0	0.004	2.981	2.986	-0.005	2.03	2.04	-0.007	0.008
136.8	4.544	4.54	0.004	0.17	0.17	0	0.004	2.998	3.002	-0.004	2.1	2.11	-0.006	0.008
135.7	4.563	4.559	0.004	0.16	0.16	0	0.004	3.018	3.022	-0.004	2.18	2.18	-0.006	0.007
134.6	4.581	4.578	0.003	0.14	0.14	0	0.003	3.041	3.044	-0.003	2.25	2.26	-0.005	0.006
133.5	4.6	4.598	0.003	0.13	0.13	0	0.003	3.068	3.071	-0.003	2.33	2.33	-0.004	0.004
132.3	4.621	4.617	0.004	0.12	0.12	0	0.004	3.099	3.102	-0.004	2.41	2.42	-0.004	0.006
131.2	4.639	4.637	0.003	0.1	0.1	0	0.003	3.137	3.14	-0.003	2.5	2.5	-0.003	0.004
130	4.66	4.656	0.003	0.09	0.09	0	0.003	3.183	3.186	-0.003	2.59	2.6	-0.003	0.005
128.9	4.678	4.676	0.002	0.07	0.07	0	0.002	3.241	3.243	-0.002	2.69	2.69	-0.002	0.003
127.7	4.699	4.696	0.002	0.06	0.06	0	0.002	3.314	3.316	-0.003	2.8	2.8	-0.002	0.003
126.6	4.717	4.717	0.001	0.05	0.05	0	0.001	3.413	3.414	-0.001	2.91	2.91	-0.001	0.001
125.4	4.738	4.737	0.001	0.03	0.03	0	0.001	3.553	3.554	-0.001	3.02	3.02	0	0.001
124.2	4.758	4.757	0.001	0.02	0.02	0	0.001	3.788	3.789	-0.001	3.14	3.14	0	0.001
123	4.779	4.778	0	0	0	0	0	4.461	4.461	-0.001	3.28	3.28	0	0.001
121.8	4.799	4.799	0	-0.01	-0.01	0	0	0	0	0	0	0	0	0
120.6	4.819	4.82	-0.001	-0.02	-0.02	0	0.001	0	0	0	0	0	0	0
119.3	4.841	4.841	0	-0.04	-0.04	0	0	0	0	0	0	0	0	0
118.1	4.862	4.863	-0.001	-0.05	-0.05	0	0.001	0	0	0	0	0	0	0
116.9	4.882	4.884	-0.002	-0.07	-0.07	0	0.002	0	0	0	0	0	0	0
115.6	4.904	4.906	-0.002	-0.08	-0.08	0	0.002	0	0	0	0	0	0	0
114.3	4.926	4.928	-0.001	-0.09	-0.09	0	0.001	0	0	0	0	0	0	0
113.1	4.947	4.95	-0.003	-0.11	-0.11	0	0.003	0	0	0	0	0	0	0
111.8	4.969	4.972	-0.003	-0.12	-0.12	0	0.003	0	0	0	0	0	0	0
110.5	4.991	4.994	-0.003	-0.14	-0.14	0	0.003	0	0	0	0	0	0	0
109.2	5.013	5.016	-0.003	-0.15	-0.15	0	0.003	0	0	0	0	0	0	0
107.9	5.035	5.038	-0.003	-0.16	-0.16	0	0.003	0	0	0	0	0	0	0
106.6	5.057	5.06	-0.003	-0.18	-0.18	0	0.003	0	0	0	0	0	0	0
105.3	5.079	5.082	-0.003	-0.19	-0.19	0	0.003	0	0	0	0	0	0	0
104	5.101	5.104	-0.003	-0.21	-0.21	0	0.003	0	0	0	0	0	0	0
102.7	5.123	5.126	-0.003	-0.22	-0.22	0	0.003	0	0	0	0	0	0	0
101.3	5.147	5.148	-0.001	-0.24	-0.24	0	0.001	0	0	0	0	0	0	0
100	5.169	5.17	0	-0.25	-0.25	0	0	0	0	0	0	0	0	0
98.5	5.195	5.191	0.003	-0.26	-0.26	0	0.003	0	0	0	0	0	0	0
97.2	5.217	5.213	0.004	-0.28	-0.28	0	0.004	0	0	0	0	0	0	0
95.9	5.239	5.234	0.005	-0.29	-0.29	0	0.005	0	0	0	0	0	0	0
94.5	5.263	5.256	0.007	-0.31	-0.31	0	0.007	0	0	0	0	0	0	0

AVERA F SUM QUARES

OF RESIDL 1 2.9E-06 1 1.7E-07 1.4E-05 1 6.9E-06 3 6.6E-06 5.4E-05

NUMBEF TITRONS = 1

TOTAL BER OFNTS = 130

Appendix 7: Determination of Cr^{III}-Bpy stability constants (+CrOH) L_T:M_T ratio 4

TASK ZBAR BYP 0 COMES WIT Cr(III) ratio 4

MODL Cr+3 BYP0 H 1

CPLX 0 0 -13.800 H+1(-1)

CPLX 0 0 -4.920 BY0(1) H+1(1)

CPLX 0 0 -4.000 Cr-3(1) H+1(-1)

CPLX 1 0 2.100 Cr-3(1) B'P0(1)

CPLX 1 0 4.680 Cr-3(1) B'P0(2)

CPLX 1 0 -1.450 Cr-3(1) B'P0(1) H+1(-1)

CPLX 1 0 -6.780 Cr-3(1) B'P0(1) H+1(-2)

CPLX 1 0 -13.400 Cr-3(1) B'P0(1) H+1(-3)

CONC

VESL IVOL 0.000 C 0

VESL H+1 C 1E+05 0 0

VESL Cr+3 C 20176 0 0

VESL BYP0 81798 0 0

BUR1 H+1 -C 2E+05 0 0

ELEC

ZERO H+1 5.02 0

GRAD H+1 8.66 0

DATA

0	EMF	PH			ZBAR(H)			POINT	PA			ZBAR(M)			POINT
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID	
238.3	2.842	2.864	-0.022	0.94	0.95	-0.009	0.023	3.801	3.775	0.026	0.14	0.09	0.043	0.05	
236.7	2.869	2.89	-0.02	0.94	0.95	-0.008	0.022	3.777	3.753	0.024	0.14	0.1	0.039	0.046	
235.1	2.897	2.916	-0.02	0.94	0.95	-0.008	0.021	3.752	3.729	0.023	0.14	0.11	0.036	0.043	
233.4	2.926	2.944	-0.018	0.94	0.95	-0.007	0.019	3.726	3.705	0.021	0.14	0.11	0.032	0.039	
231.6	2.956	2.972	-0.016	0.94	0.94	-0.005	0.017	3.699	3.68	0.018	0.15	0.12	0.027	0.032	
229.9	2.985	3.001	-0.016	0.93	0.94	-0.005	0.017	3.673	3.655	0.018	0.15	0.13	0.026	0.031	
228	3.018	3.031	-0.013	0.93	0.93	-0.004	0.014	3.644	3.629	0.015	0.16	0.14	0.02	0.025	
226.1	3.05	3.061	-0.011	0.93	0.93	-0.003	0.011	3.615	3.603	0.012	0.16	0.15	0.016	0.021	
224.2	3.083	3.092	-0.009	0.92	0.92	-0.002	0.01	3.587	3.576	0.01	0.17	0.16	0.013	0.017	
222.2	3.117	3.123	-0.006	0.92	0.92	-0.002	0.007	3.557	3.549	0.007	0.18	0.17	0.009	0.012	
220.2	3.151	3.155	-0.004	0.91	0.91	-0.001	0.004	3.527	3.522	0.004	0.18	0.18	0.005	0.007	
218.2	3.185	3.186	-0.002	0.91	0.91	0	0.002	3.497	3.495	0.002	0.19	0.19	0.002	0.003	
216.2	3.219	3.218	0	0.9	0.9	0	0	3.468	3.468	-0.001	0.2	0.2	-0.001	0.001	
214.2	3.253	3.25	0.003	0.9	0.89	0	0.003	3.439	3.442	-0.003	0.22	0.22	-0.003	0.004	
212.2	3.287	3.282	0.005	0.89	0.89	0.001	0.005	3.41	3.415	-0.005	0.23	0.23	-0.006	0.008	
210.2	3.321	3.314	0.007	0.88	0.88	0.001	0.007	3.381	3.389	-0.008	0.24	0.25	-0.009	0.012	
208.3	3.354	3.345	0.008	0.87	0.87	0.001	0.008	3.355	3.364	-0.009	0.26	0.27	-0.01	0.014	
206.4	3.386	3.376	0.01	0.86	0.86	0.001	0.01	3.328	3.339	-0.011	0.27	0.29	-0.012	0.016	
204.6	3.417	3.407	0.01	0.86	0.85	0.001	0.01	3.304	3.314	-0.011	0.29	0.3	-0.012	0.016	
202.8	3.447	3.437	0.011	0.85	0.85	0.001	0.011	3.28	3.291	-0.011	0.31	0.32	-0.013	0.018	
201	3.478	3.466	0.012	0.84	0.84	0.001	0.012	3.255	3.268	-0.013	0.33	0.34	-0.015	0.02	
199.4	3.505	3.495	0.01	0.83	0.83	0.001	0.01	3.235	3.246	-0.011	0.35	0.36	-0.013	0.017	
197.8	3.533	3.523	0.009	0.82	0.82	0.001	0.009	3.215	3.225	-0.01	0.37	0.38	-0.012	0.016	
196.2	3.56	3.551	0.009	0.81	0.81	0.001	0.009	3.195	3.204	-0.009	0.4	0.41	-0.012	0.015	
194.7	3.585	3.578	0.007	0.8	0.8	0.001	0.007	3.177	3.184	-0.008	0.42	0.43	-0.01	0.012	
193.1	3.613	3.605	0.008	0.79	0.79	0.001	0.008	3.157	3.165	-0.008	0.44	0.45	-0.011	0.014	
191.7	3.637	3.631	0.006	0.78	0.78	0	0.006	3.141	3.147	-0.006	0.47	0.47	-0.008	0.01	
190.3	3.66	3.656	0.004	0.77	0.77	0	0.004	3.125	3.129	-0.005	0.49	0.5	-0.006	0.008	
188.8	3.686	3.681	0.005	0.75	0.75	0	0.005	3.107	3.112	-0.005	0.51	0.52	-0.007	0.009	
187.6	3.706	3.705	0.001	0.74	0.74	0	0.001	3.095	3.096	-0.001	0.54	0.55	-0.002	0.002	
186.2	3.73	3.729	0.001	0.73	0.73	0	0.001	3.079	3.08	-0.001	0.57	0.57	-0.002	0.002	

184.9	3.752	3.753	0	0.72	0.72	0	0	3.066	3.065	0	0.6	0.6	0	0
183.6	3.775	3.776	-0.001	0.71	0.71	0	0.001	3.052	3.051	0.001	0.62	0.62	0.002	0.002
182.3	3.797	3.798	-0.002	0.7	0.7	0	0.002	3.039	3.037	0.002	0.65	0.65	0.003	0.003
181.1	3.817	3.821	-0.003	0.69	0.69	0	0.003	3.027	3.023	0.004	0.68	0.67	0.006	0.007
179.8	3.839	3.843	-0.003	0.68	0.68	0	0.003	3.014	3.011	0.003	0.7	0.7	0.005	0.006
178.6	3.86	3.864	-0.004	0.66	0.66	0	0.004	3.003	2.998	0.004	0.73	0.73	0.007	0.008
177.4	3.88	3.885	-0.005	0.65	0.65	0	0.005	2.992	2.986	0.005	0.76	0.75	0.009	0.01
176.2	3.901	3.906	-0.005	0.64	0.64	0	0.005	2.981	2.975	0.006	0.79	0.78	0.009	0.011
174.9	3.923	3.927	-0.004	0.63	0.63	0	0.004	2.968	2.964	0.004	0.82	0.81	0.007	0.008
173.8	3.942	3.947	-0.005	0.62	0.62	0	0.005	2.959	2.954	0.006	0.85	0.84	0.01	0.011
172.6	3.962	3.967	-0.005	0.61	0.61	0	0.005	2.949	2.944	0.005	0.87	0.86	0.009	0.011
171.4	3.983	3.987	-0.004	0.59	0.59	0	0.004	2.939	2.934	0.004	0.9	0.89	0.008	0.01
170.3	4.001	4.007	-0.005	0.58	0.58	0	0.005	2.93	2.925	0.005	0.93	0.92	0.01	0.012
169.1	4.022	4.026	-0.004	0.57	0.57	0	0.004	2.921	2.916	0.004	0.96	0.95	0.008	0.009
167.9	4.042	4.045	-0.003	0.56	0.56	0	0.003	2.911	2.908	0.003	0.99	0.98	0.006	0.007
166.8	4.061	4.064	-0.003	0.55	0.55	0	0.003	2.903	2.9	0.003	1.02	1.01	0.007	0.007
165.7	4.08	4.083	-0.003	0.53	0.53	0	0.003	2.896	2.892	0.003	1.05	1.04	0.007	0.008
164.5	4.1	4.102	-0.002	0.52	0.52	0	0.002	2.887	2.885	0.002	1.08	1.08	0.003	0.004
163.5	4.117	4.12	-0.003	0.51	0.51	0	0.003	2.881	2.878	0.003	1.11	1.11	0.007	0.007
162.4	4.136	4.139	-0.003	0.5	0.5	0	0.003	2.875	2.872	0.003	1.15	1.14	0.006	0.007
161.2	4.156	4.157	-0.001	0.49	0.49	0	0.001	2.867	2.866	0.001	1.17	1.17	0.001	0.002
160.2	4.174	4.175	-0.002	0.47	0.47	0	0.002	2.862	2.86	0.002	1.21	1.21	0.004	0.004
159.1	4.192	4.193	-0.001	0.46	0.46	0	0.001	2.856	2.855	0.001	1.24	1.24	0.003	0.003
158	4.211	4.211	0	0.45	0.45	0	0	2.851	2.85	0	1.28	1.28	0.001	0.001
157	4.228	4.229	-0.001	0.44	0.44	0	0.001	2.847	2.846	0.001	1.32	1.31	0.003	0.003
155.9	4.247	4.247	0	0.43	0.43	0	0	2.842	2.842	0	1.35	1.35	0.001	0.001
154.8	4.266	4.265	0.001	0.41	0.41	0	0.001	2.838	2.838	-0.001	1.39	1.39	-0.001	0.002
153.8	4.283	4.283	0	0.4	0.4	0	0	2.835	2.835	0	1.43	1.43	0	0
152.8	4.3	4.3	-0.001	0.39	0.39	0	0.001	2.833	2.832	0.001	1.47	1.47	0.002	0.002
151.7	4.318	4.318	0	0.38	0.38	0	0	2.83	2.83	0	1.51	1.51	-0.001	0.001
150.7	4.335	4.336	0	0.36	0.36	0	0	2.829	2.829	0	1.55	1.55	0.001	0.001
149.7	4.353	4.353	-0.001	0.35	0.35	0	0.001	2.828	2.827	0.001	1.59	1.59	0.002	0.002
148.6	4.371	4.371	0	0.34	0.34	0	0	2.826	2.827	0	1.64	1.64	-0.001	0.001
147.6	4.388	4.389	0	0.33	0.33	0	0	2.827	2.827	0	1.68	1.68	0.001	0.001
146.6	4.405	4.406	-0.001	0.31	0.31	0	0.001	2.828	2.827	0.001	1.73	1.73	0.002	0.002
145.5	4.424	4.424	0	0.3	0.3	0	0	2.828	2.828	0	1.78	1.78	-0.001	0.001
144.5	4.441	4.441	0	0.29	0.29	0	0	2.831	2.83	0	1.83	1.83	0.001	0.001
143.4	4.46	4.459	0.001	0.28	0.28	0	0.001	2.832	2.833	-0.001	1.88	1.88	-0.002	0.002
142.4	4.477	4.477	0	0.27	0.27	0	0	2.836	2.837	0	1.94	1.94	0	0
141.3	4.496	4.495	0.001	0.25	0.25	0	0.001	2.84	2.841	-0.001	1.99	1.99	-0.003	0.003
140.3	4.513	4.512	0	0.24	0.24	0	0	2.846	2.846	0	2.05	2.05	-0.001	0.001
139.2	4.532	4.53	0.001	0.23	0.23	0	0.001	2.851	2.853	-0.001	2.11	2.12	-0.003	0.003
138.2	4.549	4.548	0	0.22	0.22	0	0	2.86	2.86	0	2.18	2.18	-0.001	0.001
137.2	4.566	4.566	-0.001	0.2	0.2	0	0.001	2.87	2.869	0.001	2.25	2.25	0.002	0.002
136.1	4.584	4.584	0	0.19	0.19	0	0	2.88	2.88	0	2.32	2.32	0	0
135	4.603	4.603	0	0.18	0.18	0	0	2.892	2.892	0	2.39	2.39	-0.001	0.001
133.9	4.622	4.621	0.001	0.17	0.17	0	0.001	2.906	2.906	-0.001	2.47	2.47	-0.002	0.002
132.8	4.641	4.639	0.001	0.15	0.15	0	0.001	2.922	2.923	-0.001	2.55	2.55	-0.002	0.003
131.7	4.659	4.658	0.001	0.14	0.14	0	0.001	2.941	2.942	-0.001	2.63	2.63	-0.003	0.003
130.6	4.678	4.677	0.001	0.13	0.13	0	0.001	2.963	2.965	-0.001	2.72	2.72	-0.003	0.003
129.5	4.697	4.696	0.001	0.12	0.12	0	0.001	2.99	2.991	-0.001	2.82	2.82	-0.002	0.003
128.4	4.716	4.715	0.001	0.1	0.1	0	0.001	3.021	3.022	-0.001	2.92	2.92	-0.002	0.002
127.2	4.736	4.734	0.002	0.09	0.09	0	0.002	3.057	3.059	-0.002	3.02	3.03	-0.003	0.004
126.1	4.755	4.753	0.001	0.08	0.08	0	0.001	3.102	3.103	-0.002	3.14	3.14	-0.002	0.003
124.9	4.775	4.773	0.002	0.07	0.07	0	0.002	3.156	3.159	-0.002	3.25	3.26	-0.003	0.004
123.8	4.794	4.793	0.001	0.06	0.06	0	0.001	3.227	3.228	-0.001	3.38	3.38	-0.001	0.002

122.6	4.815	4.813	0.002	0.04	0.04	0	0.002	3.319	3.321	-0.002	3.52	3.52	-0.002	0.002
121.4	4.835	4.833	0.002	0.03	0.03	0	0.002	3.449	3.451	-0.002	3.66	3.66	-0.001	0.002
120.2	4.855	4.854	0.002	0.02	0.02	0	0.002	3.66	3.662	-0.002	3.81	3.82	-0.001	0.002
119	4.876	4.874	0.002	0.01	0.01	0	0.002	4.16	4.162	-0.002	3.98	3.98	0	0.002
117.7	4.898	4.895	0.003	-0.01	-0.01	0	0.003	0	0	0	0	0	0	0
116.6	4.917	4.917	0	-0.02	-0.02	0	0	0	0	0	0	0	0	0
115.3	4.939	4.938	0.001	-0.03	-0.03	0	0.001	0	0	0	0	0	0	0
114	4.961	4.96	0.001	-0.04	-0.04	0	0.001	0	0	0	0	0	0	0
112.7	4.983	4.982	0.001	-0.06	-0.06	0	0.001	0	0	0	0	0	0	0
111.4	5.005	5.004	0.001	-0.07	-0.07	0	0.001	0	0	0	0	0	0	0
110.1	5.028	5.027	0	-0.08	-0.08	0	0	0	0	0	0	0	0	0
108.8	5.05	5.05	-0.001	-0.09	-0.09	0	0.001	0	0	0	0	0	0	0
107.5	5.072	5.074	-0.002	-0.11	-0.11	0	0.002	0	0	0	0	0	0	0
106.1	5.096	5.097	-0.002	-0.12	-0.12	0	0.002	0	0	0	0	0	0	0
104.7	5.12	5.122	-0.002	-0.13	-0.13	0	0.002	0	0	0	0	0	0	0
103.3	5.144	5.146	-0.002	-0.14	-0.14	0	0.002	0	0	0	0	0	0	0
101.9	5.167	5.171	-0.003	-0.16	-0.16	0	0.003	0	0	0	0	0	0	0
100.4	5.193	5.196	-0.003	-0.17	-0.17	0	0.003	0	0	0	0	0	0	0
98.9	5.219	5.221	-0.003	-0.18	-0.18	0	0.003	0	0	0	0	0	0	0
97.4	5.244	5.247	-0.003	-0.19	-0.19	0	0.003	0	0	0	0	0	0	0
95.9	5.27	5.273	-0.003	-0.21	-0.21	0	0.003	0	0	0	0	0	0	0
94.3	5.297	5.299	-0.002	-0.22	-0.22	0	0.002	0	0	0	0	0	0	0
92.7	5.324	5.326	-0.002	-0.23	-0.23	0	0.002	0	0	0	0	0	0	0
91.1	5.352	5.353	-0.001	-0.24	-0.24	0	0.001	0	0	0	0	0	0	0
89.4	5.38	5.38	0	-0.26	-0.26	0	0	0	0	0	0	0	0	0
87.8	5.408	5.407	0	-0.27	-0.27	0	0	0	0	0	0	0	0	0
86	5.438	5.435	0.003	-0.28	-0.28	0	0.003	0	0	0	0	0	0	0
84.3	5.467	5.463	0.004	-0.29	-0.29	0	0.004	0	0	0	0	0	0	0
82.7	5.495	5.491	0.003	-0.31	-0.31	0	0.003	0	0	0	0	0	0	0
81.2	5.52	5.52	0.001	-0.32	-0.32	0	0.001	0	0	0	0	0	0	0
79.9	5.542	5.548	-0.006	-0.33	-0.33	0	0.006	0	0	0	0	0	0	0

AVERA F SUM QUARES

OF	RESIDU	3	4.8E-06	3	7.0E-08	3.8E-05	5	5.4E-06	1	2.0E-05	1.8E-04
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NUMBE F TITR ONS = 1

TOTAL BER OFNTS = 118

Appendix 8: Determination of Cr^{III}-Bpy stability constants (+CrOH) L_T:M_T ratio 9

TASK ZBAR BYP 0 COMES WIT Cr(III) ratio 9

MODL Cr+3 BYP0 H 1

CPLX 0 0 -13 800 H+1(-1)

CPLX 0 0 -4.920 BY0(1) H+1(1)

CPLX 0 0 -4.000 Cr-3(1) H+1(-1)

CPLX 1 0 1.760 Cr-3(1) B'P0(1)

CPLX 1 0 -1.860 Cr-3(1) B'P0(1) H+1(- 1)

CPLX 1 0 -6.850 Cr-3(1) B'P0(1) H+1(- 2)

CPLX 1 0 -13 500 Cr-3(1) B'P0(1) H+1(- 3)

CONC

VESL IVOL 0.000 C 0

VESL H+1 C 1E+05 0 0

VESL Cr+3 C 10028 0 0

VESL BYP0 92023 0 0

BUR1 H+1 -C 2E+05 0 0

ELEC

ZERO H+1 5.49 0

GRAD H+1 8.801 0

DATA

0 EMF		PH		ZBAR(H)			POINT		PA			ZBAR(M)			POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID		
236.3	2.877	2.89	-0.012	0.96	0.96	-0.004	0.013	3.692	3.677	0.014	0.15	0.11	0.047	0.049		
234.5	2.908	2.918	-0.01	0.96	0.96	-0.003	0.011	3.664	3.652	0.012	0.15	0.11	0.037	0.039		
232.7	2.939	2.948	-0.009	0.96	0.96	-0.003	0.01	3.636	3.626	0.011	0.15	0.12	0.032	0.034		
230.9	2.969	2.978	-0.009	0.95	0.96	-0.003	0.01	3.609	3.599	0.01	0.16	0.13	0.03	0.032		
228.9	3.003	3.01	-0.006	0.95	0.95	-0.002	0.007	3.578	3.571	0.007	0.16	0.14	0.02	0.022		
227	3.035	3.042	-0.006	0.95	0.95	-0.002	0.006	3.549	3.542	0.007	0.17	0.15	0.019	0.02		
224.9	3.071	3.075	-0.003	0.95	0.95	-0.001	0.003	3.517	3.513	0.004	0.17	0.16	0.01	0.011		
222.9	3.105	3.108	-0.003	0.94	0.94	-0.001	0.003	3.487	3.484	0.003	0.19	0.18	0.008	0.009		
220.8	3.141	3.142	-0.001	0.94	0.94	0	0.001	3.455	3.454	0.001	0.2	0.19	0.003	0.003		
218.8	3.175	3.176	-0.001	0.93	0.93	0	0.001	3.425	3.424	0.001	0.21	0.21	0.004	0.004		
216.7	3.211	3.211	0	0.93	0.93	0	0	3.394	3.394	0	0.23	0.23	0	0		
214.5	3.248	3.245	0.003	0.92	0.92	0	0.003	3.361	3.364	-0.003	0.24	0.25	-0.007	0.008		
212.5	3.282	3.28	0.002	0.92	0.91	0	0.002	3.332	3.334	-0.002	0.26	0.27	-0.006	0.007		
210.4	3.318	3.314	0.004	0.91	0.91	0.001	0.004	3.301	3.305	-0.004	0.28	0.29	-0.01	0.011		
208.4	3.352	3.348	0.004	0.9	0.9	0.001	0.004	3.272	3.277	-0.004	0.3	0.31	-0.011	0.012		
206.5	3.384	3.381	0.003	0.89	0.89	0	0.003	3.246	3.249	-0.003	0.33	0.34	-0.008	0.009		
204.5	3.418	3.414	0.005	0.89	0.89	0.001	0.005	3.217	3.222	-0.005	0.35	0.37	-0.012	0.013		
202.7	3.449	3.445	0.003	0.88	0.88	0	0.003	3.193	3.196	-0.003	0.39	0.39	-0.009	0.009		
200.8	3.481	3.477	0.004	0.87	0.87	0	0.004	3.166	3.171	-0.005	0.41	0.42	-0.012	0.013		
199	3.512	3.507	0.004	0.86	0.86	0	0.004	3.142	3.146	-0.005	0.44	0.45	-0.012	0.013		
197.3	3.541	3.537	0.004	0.85	0.85	0	0.004	3.119	3.123	-0.004	0.47	0.48	-0.01	0.011		
195.6	3.569	3.566	0.003	0.84	0.84	0	0.003	3.097	3.1	-0.004	0.51	0.52	-0.01	0.011		
194	3.597	3.594	0.002	0.83	0.83	0	0.002	3.076	3.079	-0.003	0.54	0.55	-0.007	0.008		
192.4	3.624	3.622	0.002	0.83	0.83	0	0.002	3.056	3.058	-0.002	0.58	0.58	-0.006	0.007		
190.9	3.649	3.649	0.001	0.82	0.82	0	0.001	3.037	3.038	-0.001	0.61	0.62	-0.002	0.002		
189.3	3.677	3.675	0.002	0.81	0.81	0	0.002	3.017	3.019	-0.002	0.65	0.65	-0.005	0.006		
187.9	3.7	3.701	0	0.8	0.8	0	0	3	3	0	0.69	0.69	0.001	0.001		
186.4	3.726	3.726	0	0.79	0.79	0	0	2.982	2.982	0	0.72	0.72	-0.001	0.001		
185	3.75	3.75	0	0.78	0.78	0	0	2.965	2.965	0	0.76	0.76	0.001	0.001		
183.7	3.772	3.774	-0.002	0.77	0.77	0	0.002	2.951	2.949	0.002	0.8	0.79	0.008	0.008		
182.3	3.796	3.798	-0.002	0.76	0.76	0	0.002	2.935	2.933	0.002	0.84	0.83	0.007	0.007		
180.9	3.819	3.821	-0.001	0.75	0.75	0	0.001	2.918	2.917	0.001	0.87	0.87	0.004	0.004		

179.6	3.842	3.843	-0.002	0.74	0.74	0	0.002	2.904	2.903	0.002	0.91	0.9	0.006	0.006
178.4	3.862	3.865	-0.003	0.73	0.73	0	0.003	2.892	2.888	0.003	0.96	0.94	0.013	0.014
177	3.886	3.887	-0.001	0.72	0.72	0	0.001	2.876	2.874	0.001	0.98	0.98	0.005	0.006
175.8	3.906	3.909	-0.002	0.71	0.71	0	0.002	2.864	2.861	0.002	1.03	1.02	0.01	0.01
174.5	3.928	3.93	-0.001	0.69	0.69	0	0.001	2.85	2.848	0.001	1.06	1.05	0.006	0.006
173.3	3.949	3.95	-0.002	0.68	0.68	0	0.002	2.838	2.836	0.002	1.1	1.09	0.008	0.008
172.1	3.969	3.971	-0.002	0.67	0.67	0	0.002	2.826	2.824	0.002	1.14	1.13	0.008	0.009
170.9	3.99	3.991	-0.002	0.66	0.66	0	0.002	2.814	2.812	0.002	1.18	1.17	0.008	0.008
169.7	4.01	4.011	-0.001	0.65	0.65	0	0.001	2.802	2.801	0.001	1.21	1.21	0.006	0.006
168.5	4.03	4.031	-0.001	0.64	0.64	0	0.001	2.791	2.79	0.001	1.25	1.25	0.003	0.003
167.4	4.049	4.05	-0.001	0.63	0.63	0	0.001	2.781	2.779	0.001	1.29	1.29	0.007	0.007
166.2	4.069	4.07	0	0.62	0.62	0	0	2.77	2.769	0	1.33	1.33	0.002	0.002
165	4.09	4.089	0.001	0.61	0.61	0	0.001	2.758	2.759	-0.001	1.36	1.37	-0.005	0.005
163.9	4.109	4.108	0.001	0.6	0.6	0	0.001	2.749	2.75	-0.001	1.4	1.41	-0.003	0.004
162.8	4.127	4.127	0.001	0.59	0.59	0	0.001	2.74	2.74	-0.001	1.44	1.45	-0.003	0.003
161.7	4.146	4.145	0.001	0.58	0.58	0	0.001	2.731	2.731	-0.001	1.48	1.49	-0.003	0.003
160.6	4.165	4.164	0.001	0.57	0.57	0	0.001	2.722	2.723	-0.001	1.52	1.53	-0.004	0.004
159.6	4.182	4.182	-0.001	0.56	0.56	0	0.001	2.715	2.714	0.001	1.57	1.57	0.004	0.004
158.5	4.2	4.201	0	0.55	0.55	0	0	2.707	2.706	0	1.61	1.61	0.002	0.002
157.4	4.219	4.219	0	0.53	0.53	0	0	2.698	2.698	0	1.65	1.65	-0.001	0.001
156.3	4.238	4.237	0.001	0.52	0.52	0	0.001	2.69	2.691	-0.001	1.69	1.7	-0.005	0.005
155.3	4.255	4.255	0	0.51	0.51	0	0	2.684	2.684	0	1.74	1.74	0.002	0.002
154.2	4.274	4.273	0	0.5	0.5	0	0	2.676	2.677	0	1.78	1.79	-0.003	0.003
153.1	4.292	4.291	0.001	0.49	0.49	0	0.001	2.668	2.67	-0.001	1.82	1.83	-0.009	0.009
152.1	4.309	4.309	0	0.48	0.48	0	0	2.663	2.663	0	1.88	1.88	-0.003	0.003
151.1	4.326	4.327	0	0.47	0.47	0	0	2.657	2.657	0	1.93	1.93	0.003	0.003
150	4.345	4.344	0.001	0.46	0.46	0	0.001	2.651	2.651	-0.001	1.97	1.97	-0.004	0.004
148.9	4.364	4.362	0.001	0.45	0.45	0	0.001	2.644	2.645	-0.001	2.01	2.02	-0.011	0.011
147.9	4.381	4.38	0.001	0.44	0.44	0	0.001	2.639	2.64	-0.001	2.07	2.07	-0.005	0.005
146.9	4.398	4.398	0	0.43	0.43	0	0	2.635	2.635	0	2.13	2.13	0	0
145.8	4.416	4.416	0.001	0.41	0.41	0	0.001	2.629	2.63	-0.001	2.17	2.18	-0.007	0.007
144.8	4.433	4.433	0	0.4	0.4	0	0	2.625	2.625	0	2.23	2.23	-0.001	0.001
143.7	4.452	4.451	0.001	0.39	0.39	0	0.001	2.62	2.621	-0.001	2.28	2.29	-0.007	0.007
142.7	4.469	4.469	0	0.38	0.38	0	0	2.617	2.617	0	2.35	2.35	-0.001	0.001
141.6	4.488	4.487	0.001	0.37	0.37	0	0.001	2.612	2.613	-0.001	2.4	2.41	-0.007	0.007
140.6	4.505	4.505	0	0.36	0.36	0	0	2.61	2.61	0	2.47	2.47	0.001	0.001
139.5	4.524	4.523	0.001	0.35	0.35	0	0.001	2.606	2.607	-0.001	2.53	2.53	-0.004	0.004
138.5	4.541	4.541	-0.001	0.34	0.34	0	0.001	2.605	2.604	0.001	2.61	2.6	0.005	0.005
137.4	4.559	4.559	0	0.33	0.33	0	0	2.602	2.602	0	2.67	2.67	0.001	0.001
136.3	4.578	4.578	0	0.32	0.32	0	0	2.6	2.6	0	2.74	2.74	-0.002	0.002
135.2	4.597	4.596	0	0.3	0.3	0	0	2.598	2.598	0	2.82	2.82	-0.004	0.004
134.1	4.615	4.615	0.001	0.29	0.29	0	0.001	2.597	2.597	-0.001	2.89	2.9	-0.004	0.004
133	4.634	4.634	0	0.28	0.28	0	0	2.596	2.597	0	2.98	2.98	-0.004	0.004
131.9	4.653	4.653	0	0.27	0.27	0	0	2.596	2.596	0	3.07	3.07	-0.002	0.002
130.8	4.672	4.672	0	0.26	0.26	0	0	2.597	2.597	0	3.16	3.16	0.002	0.002
129.7	4.69	4.691	-0.001	0.25	0.25	0	0.001	2.598	2.598	0.001	3.26	3.26	0.007	0.007
128.5	4.711	4.711	0	0.24	0.24	0	0	2.599	2.599	0	3.36	3.36	-0.001	0.001
127.3	4.731	4.73	0.001	0.23	0.23	0	0.001	2.601	2.601	-0.001	3.46	3.47	-0.006	0.006
126.1	4.751	4.75	0.001	0.22	0.22	0	0.001	2.603	2.605	-0.001	3.57	3.58	-0.009	0.01
125	4.77	4.771	0	0.21	0.21	0	0	2.609	2.608	0	3.71	3.7	0.004	0.004
123.7	4.792	4.791	0.001	0.19	0.19	0	0.001	2.612	2.613	-0.001	3.82	3.83	-0.009	0.009
122.5	4.813	4.812	0.001	0.18	0.18	0	0.001	2.619	2.619	-0.001	3.96	3.97	-0.005	0.005
121.3	4.833	4.833	0	0.17	0.17	0	0	2.627	2.626	0	4.12	4.12	0.002	0.002
120	4.855	4.855	0	0.16	0.16	0	0	2.635	2.635	0	4.27	4.27	-0.002	0.002
118.7	4.877	4.877	0	0.15	0.15	0	0	2.645	2.645	0	4.44	4.44	-0.003	0.003
117.3	4.901	4.899	0.002	0.14	0.14	0	0.002	2.656	2.657	-0.002	4.61	4.63	-0.014	0.014

116.1	4.922	4.922	-0.001	0.13	0.13	0	0.001	2.673	2.672	0.001	4.83	4.82	0.005	0.005
114.7	4.945	4.946	0	0.12	0.12	0	0	2.689	2.689	0	5.04	5.04	0.001	0.001
113.3	4.969	4.969	0	0.11	0.11	0	0	2.71	2.71	0	5.27	5.27	0.002	0.002
111.8	4.995	4.994	0.001	0.1	0.1	0	0.001	2.734	2.734	-0.001	5.52	5.53	-0.005	0.005
110.4	5.018	5.019	0	0.08	0.08	0	0	2.765	2.764	0	5.81	5.81	0.002	0.002
108.9	5.044	5.045	-0.001	0.07	0.07	0	0.001	2.802	2.801	0.001	6.11	6.11	0.003	0.003
107.4	5.069	5.071	-0.001	0.06	0.06	0	0.001	2.849	2.848	0.001	6.46	6.45	0.007	0.007
105.9	5.095	5.098	-0.003	0.05	0.05	0	0.003	2.911	2.908	0.003	6.83	6.82	0.013	0.014
104.2	5.124	5.126	-0.002	0.04	0.04	0	0.002	2.99	2.988	0.002	7.24	7.24	0.007	0.008
102.6	5.151	5.155	-0.003	0.03	0.03	0	0.003	3.105	3.102	0.004	7.71	7.7	0.01	0.011
100.8	5.182	5.184	-0.003	0.02	0.02	0	0.003	3.287	3.284	0.003	8.22	8.21	0.005	0.006
99.1	5.211	5.215	-0.004	0.01	0.01	0	0.004	3.687	3.682	0.005	8.8	8.79	0.004	0.006
97.3	5.241	5.247	-0.005	0	0	0	0.005	0	0	0	0	0	0	0
95.3	5.275	5.279	-0.004	-0.02	-0.02	0	0.004	0	0	0	0	0	0	0
93.4	5.308	5.313	-0.006	-0.03	-0.03	0	0.006	0	0	0	0	0	0	0
91.3	5.343	5.348	-0.005	-0.04	-0.04	0	0.005	0	0	0	0	0	0	0
89.1	5.381	5.385	-0.004	-0.05	-0.05	0	0.004	0	0	0	0	0	0	0
86.8	5.42	5.423	-0.003	-0.06	-0.06	0	0.003	0	0	0	0	0	0	0
84.5	5.459	5.462	-0.003	-0.07	-0.07	0	0.003	0	0	0	0	0	0	0
81.9	5.503	5.503	0	-0.08	-0.08	0	0	0	0	0	0	0	0	0
79.2	5.549	5.546	0.003	-0.09	-0.09	0	0.003	0	0	0	0	0	0	0
76.4	5.597	5.59	0.006	-0.1	-0.1	0	0.006	0	0	0	0	0	0	0
73.4	5.648	5.637	0.011	-0.12	-0.12	0	0.011	0	0	0	0	0	0	0
70.4	5.699	5.685	0.014	-0.13	-0.13	0	0.014	0	0	0	0	0	0	0
67.3	5.751	5.734	0.017	-0.14	-0.14	0	0.017	0	0	0	0	0	0	0
65.3	5.785	5.786	-0.001	-0.15	-0.15	0	0.001	0	0	0	0	0	0	0
63.7	5.813	5.841	-0.028	-0.16	-0.16	0	0.028	0	0	0	0	0	0	0

AVERAGE SUM SQUARES

OF RESIDUALS 2 9.0E-07 4 6.0E-08 2.1E-05 1 0.0E+00 1 1.0E-06 1.1E-04

NUMBER OF TITRATIONS = 1

TOTAL NUMBER OF POINTS = 115

Appendix 9: Determination of Cr^{III}-Bpy stability constants (-CrOH) L_T:M_T ratio 1

TASK ZBAR BYP0 COMPLS WITI Cr(III) ratio 1 bis

MODL Cr+3 BYP0 H+1

CPLX 0 0 -13.800 H+(-1)

CPLX 0 0 4.920 BY(1) H+1(1)

CPLX 1 0 2.900 Cr(1) BY0(1)

CPLX 1 0 -1.890 Cr(1) BY0(1) H+1(-)

CPLX 1 0 -7.880 Cr(1) BY0(1) H+1(-)

CPLX 1 0 -11.000 Cr(1) BY0(1) H+1(-)

CONC

VESL IVOL 0.000 C 0

VESL H+1 0.116755 0

VESL Cr+3 0.049990 0

VESL BYP0 0.49795 0

BUR1 H+1 -0.217250 0

ELEC

ZERO H+1 5.51 0

GRAD H+1 8.987 0

DATA

0 EMF		PH		ZBAR(H)				POINT		PA		ZBAR(M)			POINT
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID	
255.7	2.54	2.537	0.003	0.97	0.97	0.005	0.006	4.331	4.336	-0.005	0.01	0.02	-0.005	0.007	
253.8	2.572	2.568	0.004	0.97	0.97	0.006	0.007	4.303	4.31	-0.007	0.01	0.02	-0.006	0.009	
251.9	2.604	2.601	0.004	0.97	0.96	0.005	0.006	4.276	4.282	-0.006	0.02	0.02	-0.005	0.008	
250	2.636	2.635	0.001	0.96	0.96	0.002	0.002	4.25	4.252	-0.002	0.02	0.02	-0.002	0.002	
247.8	2.674	2.672	0.002	0.96	0.96	0.002	0.003	4.218	4.221	-0.003	0.02	0.03	-0.002	0.004	
245.6	2.711	2.71	0.001	0.96	0.96	0.001	0.001	4.186	4.187	-0.001	0.03	0.03	-0.001	0.001	
243.2	2.752	2.752	0	0.95	0.95	0	0	4.151	4.151	0	0.03	0.03	0	0	
240.8	2.792	2.795	-0.003	0.94	0.95	-0.003	0.004	4.118	4.114	0.004	0.04	0.04	0.003	0.005	
238.1	2.838	2.842	-0.004	0.94	0.94	-0.003	0.005	4.079	4.073	0.006	0.04	0.04	0.004	0.007	
235.2	2.887	2.892	-0.005	0.93	0.93	-0.004	0.006	4.037	4.03	0.007	0.05	0.04	0.004	0.008	
232.1	2.94	2.945	-0.005	0.92	0.92	-0.004	0.006	3.992	3.985	0.007	0.05	0.05	0.004	0.008	
228.9	2.994	3.002	-0.007	0.91	0.91	-0.004	0.009	3.946	3.937	0.01	0.06	0.06	0.005	0.011	
225.4	3.053	3.061	-0.007	0.9	0.9	-0.004	0.008	3.896	3.887	0.009	0.07	0.07	0.005	0.01	
221.7	3.116	3.122	-0.006	0.88	0.88	-0.003	0.007	3.844	3.836	0.008	0.08	0.08	0.004	0.008	
217.9	3.181	3.186	-0.005	0.86	0.87	-0.002	0.005	3.792	3.786	0.006	0.09	0.09	0.003	0.007	
214	3.247	3.249	-0.003	0.84	0.84	-0.001	0.003	3.74	3.737	0.003	0.11	0.11	0.001	0.003	
210.1	3.313	3.312	0.001	0.82	0.82	0	0.001	3.689	3.69	-0.001	0.13	0.13	0	0.001	
206.3	3.377	3.373	0.004	0.79	0.79	0.001	0.004	3.642	3.647	-0.004	0.15	0.15	-0.002	0.005	
202.7	3.438	3.432	0.006	0.76	0.76	0.001	0.006	3.601	3.608	-0.007	0.17	0.17	-0.002	0.007	
199.3	3.496	3.488	0.007	0.73	0.73	0.001	0.008	3.565	3.574	-0.008	0.19	0.2	-0.003	0.009	
196	3.552	3.542	0.01	0.7	0.7	0.002	0.01	3.533	3.544	-0.011	0.22	0.23	-0.004	0.012	
193	3.603	3.592	0.01	0.66	0.66	0.002	0.01	3.508	3.52	-0.011	0.25	0.26	-0.004	0.012	
190.3	3.648	3.64	0.008	0.62	0.62	0.001	0.008	3.491	3.5	-0.009	0.28	0.29	-0.003	0.009	
187.7	3.693	3.686	0.006	0.59	0.59	0.001	0.006	3.477	3.484	-0.007	0.32	0.32	-0.002	0.007	
185.3	3.733	3.73	0.003	0.55	0.55	0	0.003	3.469	3.473	-0.004	0.36	0.36	-0.001	0.004	
183	3.772	3.772	0.001	0.51	0.51	0	0.001	3.466	3.466	-0.001	0.39	0.39	0	0.001	
180.8	3.809	3.812	-0.003	0.47	0.47	0	0.003	3.467	3.465	0.003	0.43	0.43	0.001	0.003	
178.7	3.845	3.851	-0.006	0.43	0.43	-0.001	0.006	3.474	3.468	0.006	0.47	0.47	0.002	0.007	
176.5	3.882	3.889	-0.006	0.39	0.39	-0.001	0.006	3.483	3.476	0.007	0.52	0.51	0.002	0.007	
174.4	3.918	3.926	-0.008	0.35	0.35	-0.001	0.008	3.499	3.49	0.009	0.56	0.56	0.002	0.009	
172.3	3.954	3.962	-0.008	0.31	0.31	-0.001	0.008	3.521	3.512	0.009	0.6	0.6	0.002	0.009	
170.2	3.989	3.997	-0.008	0.26	0.26	-0.001	0.008	3.552	3.543	0.009	0.65	0.65	0.002	0.009	
168.2	4.023	4.032	-0.009	0.22	0.22	-0.001	0.009	3.595	3.585	0.01	0.7	0.7	0.002	0.011	

166.1	4.059	4.067	-0.008	0.18	0.18	0	0.008	3.652	3.643	0.009	0.75	0.75	0.002	0.009
163.9	4.096	4.101	-0.005	0.14	0.14	0	0.005	3.732	3.726	0.006	0.8	0.8	0.001	0.006
161.9	4.13	4.135	-0.005	0.1	0.1	0	0.005	3.856	3.85	0.006	0.86	0.86	0.001	0.006
159.7	4.167	4.169	-0.002	0.06	0.06	0	0.002	4.067	4.065	0.003	0.92	0.91	0	0.003
157.6	4.203	4.203	0	0.01	0.01	0	0	4.659	4.658	0.001	0.98	0.98	0	0.001
155.5	4.238	4.237	0.001	-0.03	-0.03	0	0.001	0	0	0	0	0	0	0
153.3	4.276	4.272	0.004	-0.07	-0.07	0	0.004	0	0	0	0	0	0	0
151.2	4.311	4.306	0.005	-0.11	-0.11	0	0.005	0	0	0	0	0	0	0
149.1	4.347	4.341	0.006	-0.16	-0.16	0	0.006	0	0	0	0	0	0	0
146.9	4.384	4.377	0.007	-0.2	-0.2	0	0.007	0	0	0	0	0	0	0
144.9	4.418	4.413	0.005	-0.24	-0.24	0	0.005	0	0	0	0	0	0	0
142.7	4.455	4.449	0.006	-0.28	-0.28	0	0.006	0	0	0	0	0	0	0
140.7	4.489	4.486	0.004	-0.33	-0.33	0	0.004	0	0	0	0	0	0	0
138.5	4.527	4.523	0.004	-0.37	-0.37	0	0.004	0	0	0	0	0	0	0
136.3	4.564	4.561	0.003	-0.41	-0.41	0	0.003	0	0	0	0	0	0	0
134.3	4.598	4.599	-0.001	-0.46	-0.46	0	0.001	0	0	0	0	0	0	0
132.1	4.635	4.637	-0.002	-0.5	-0.5	0	0.002	0	0	0	0	0	0	0
129.9	4.672	4.675	-0.002	-0.54	-0.54	0	0.002	0	0	0	0	0	0	0
127.8	4.708	4.712	-0.004	-0.58	-0.58	0	0.004	0	0	0	0	0	0	0
125.6	4.745	4.749	-0.004	-0.63	-0.63	0	0.004	0	0	0	0	0	0	0
123.5	4.781	4.786	-0.005	-0.67	-0.67	0	0.005	0	0	0	0	0	0	0
121.4	4.816	4.821	-0.004	-0.71	-0.71	0	0.004	0	0	0	0	0	0	0
119.4	4.85	4.855	-0.004	-0.76	-0.76	0	0.004	0	0	0	0	0	0	0
117.3	4.886	4.887	-0.001	-0.8	-0.8	0	0.001	0	0	0	0	0	0	0
115.2	4.922	4.918	0.003	-0.84	-0.84	0	0.003	0	0	0	0	0	0	0
113.2	4.955	4.948	0.008	-0.89	-0.89	0	0.008	0	0	0	0	0	0	0

AVERAC OF SUI QUARES
 OF RESIDL 2 7.5E-04 3 4.0E-05 3.1E-05 4 4.4E-06 8 3.3E-07 5.3E-05

 NUMBEI OF TIT ONS = 1

 TOTAL MBER C NTS = 59

Appendix 10: Determination of Cr^{III}-Bpy stability constants (-CrOH) L_T:M_T ratio 2

TASK ZBAR BYP 0 COMP ES WI' Cr(III) ratio 2 bis

MODL Cr+3 BYP0 H 1

CPLX 0 0 -1:800 H -1(-1)

CPLX 0 0 4 920 BY0(1) H +1(1)

CPLX 1 0 2 210 Cr-3(1) BY P0(1)

CPLX 1 0 5 470 Cr-3(1) BY P0(2)

CPLX 1 0 -1 560 Cr-3(1) BY P0(1) H +1(- 1)

CPLX 1 0 -7 580 Cr-3(1) BY P0(1) H +1(- 2)

CONC

VESL IVOL 5.000 (0

VESL H +1 1E+05 0 0

VESL Cr+3 33452 0 0

VESL BYP0 67439 0 0

BUR1 H +1 - 2E+05 0 0

ELEC

ZERO H +1 4.56 0

GRAD H +1 8.972 0

DATA

0 EMF		PH		ZBAR(H)			POINT		PA		ZBAR(M)			POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID	
247.6	2.662	2.664	-0.002	0.96	0.97	-0.002	0.003	4.051	4.048	0.003	0.05	0.04	0.004	0.005	
245.8	2.692	2.692	0.001	0.96	0.96	0	0.001	4.023	4.024	-0.001	0.04	0.04	-0.001	0.001	
244.2	2.719	2.72	-0.001	0.96	0.96	-0.001	0.001	4	3.999	0.001	0.05	0.05	0.002	0.002	
242.4	2.75	2.75	0	0.96	0.96	0	0.001	3.973	3.973	0.001	0.05	0.05	0.001	0.001	
240.5	2.782	2.781	0.001	0.96	0.96	0	0.001	3.945	3.946	-0.001	0.05	0.05	-0.001	0.001	
238.7	2.813	2.814	-0.001	0.95	0.95	-0.001	0.002	3.919	3.917	0.002	0.06	0.06	0.002	0.003	
236.6	2.848	2.848	0	0.95	0.95	0	0	3.887	3.888	0	0.06	0.06	0	0	
234.4	2.885	2.884	0.002	0.94	0.94	0.001	0.002	3.854	3.857	-0.002	0.06	0.07	-0.002	0.003	
232.4	2.919	2.92	-0.001	0.94	0.94	-0.001	0.001	3.826	3.824	0.001	0.07	0.07	0.001	0.002	
230.2	2.957	2.959	-0.002	0.93	0.93	-0.001	0.002	3.794	3.791	0.003	0.08	0.08	0.002	0.004	
227.6	3.001	2.999	0.002	0.93	0.93	0.001	0.002	3.754	3.757	-0.002	0.08	0.09	-0.002	0.003	
225	3.045	3.04	0.005	0.92	0.92	0.002	0.005	3.716	3.721	-0.006	0.09	0.1	-0.005	0.007	
222.6	3.086	3.082	0.004	0.91	0.91	0.001	0.004	3.681	3.685	-0.004	0.1	0.11	-0.003	0.005	
220.3	3.125	3.125	-0.001	0.9	0.9	0	0.001	3.65	3.649	0.001	0.12	0.12	0	0.001	
217.8	3.167	3.169	-0.002	0.89	0.89	0	0.002	3.615	3.613	0.002	0.13	0.13	0.001	0.002	
215.1	3.213	3.213	0	0.88	0.88	0	0	3.576	3.576	0	0.14	0.14	0	0	
212.5	3.257	3.256	0	0.87	0.87	0	0	3.54	3.541	0	0.16	0.16	0	0	
210	3.299	3.3	-0.001	0.86	0.86	0	0.001	3.507	3.506	0.001	0.17	0.17	0.001	0.001	
207.6	3.34	3.343	-0.003	0.84	0.85	-0.001	0.003	3.476	3.473	0.003	0.19	0.19	0.002	0.004	
205	3.384	3.385	-0.001	0.83	0.83	0	0.001	3.441	3.44	0.001	0.21	0.21	0.001	0.001	
202.5	3.426	3.426	0	0.82	0.82	0	0	3.409	3.41	0	0.23	0.23	0	0	
200.3	3.464	3.466	-0.003	0.8	0.8	0	0.003	3.383	3.38	0.003	0.25	0.25	0.002	0.003	
197.9	3.504	3.505	-0.001	0.78	0.78	0	0.001	3.354	3.353	0.001	0.28	0.27	0.001	0.001	
195.6	3.543	3.543	0	0.77	0.77	0	0	3.326	3.327	0	0.3	0.3	0	0	
193.4	3.581	3.58	0.001	0.75	0.75	0	0.001	3.302	3.302	-0.001	0.32	0.32	-0.001	0.001	
191.3	3.616	3.616	0.001	0.73	0.73	0	0.001	3.279	3.279	-0.001	0.35	0.35	0	0.001	
189.3	3.65	3.65	0	0.71	0.71	0	0	3.258	3.258	0	0.37	0.37	0	0	
187.2	3.686	3.684	0.001	0.69	0.69	0	0.002	3.236	3.238	-0.002	0.4	0.4	-0.001	0.002	
185.3	3.718	3.717	0.001	0.68	0.68	0	0.001	3.218	3.219	-0.001	0.43	0.43	-0.001	0.001	
183.3	3.752	3.749	0.003	0.66	0.66	0	0.003	3.199	3.202	-0.003	0.45	0.45	-0.002	0.003	
181.6	3.781	3.781	0	0.64	0.64	0	0	3.186	3.186	0	0.48	0.48	0	0	
179.7	3.813	3.812	0.001	0.62	0.62	0	0.001	3.169	3.171	-0.001	0.51	0.51	-0.001	0.002	
178.1	3.84	3.842	-0.002	0.6	0.6	0	0.002	3.158	3.157	0.002	0.54	0.54	0.001	0.002	

176.3	3.871	3.871	-0.001	0.58	0.58	0	0.001	3.145	3.144	0.001	0.57	0.57	0	0.001
174.6	3.899	3.9	-0.001	0.56	0.56	0	0.001	3.133	3.133	0.001	0.6	0.6	0.001	0.001
172.9	3.928	3.929	0	0.54	0.54	0	0	3.123	3.122	0	0.64	0.64	0	0.001
171.2	3.957	3.957	0	0.52	0.52	0	0	3.112	3.113	0	0.67	0.67	0	0
169.6	3.984	3.984	0	0.5	0.5	0	0	3.105	3.105	0	0.7	0.7	0	0
168	4.011	4.012	0	0.48	0.48	0	0	3.098	3.098	0	0.74	0.74	0	0.001
166.4	4.039	4.039	0	0.46	0.46	0	0	3.092	3.092	0	0.77	0.77	0	0
164.8	4.066	4.066	0	0.44	0.44	0	0	3.087	3.087	0	0.81	0.81	0	0
163.2	4.093	4.092	0.001	0.42	0.42	0	0.001	3.083	3.084	-0.001	0.84	0.84	-0.001	0.001
161.7	4.118	4.118	0	0.4	0.4	0	0	3.082	3.082	0	0.88	0.88	0	0
160.1	4.145	4.144	0.001	0.37	0.37	0	0.001	3.08	3.081	-0.001	0.92	0.92	-0.001	0.001
158.6	4.171	4.17	0.001	0.35	0.35	0	0.001	3.081	3.082	-0.001	0.96	0.96	-0.001	0.001
157.1	4.196	4.196	0	0.33	0.33	0	0	3.084	3.085	0	1	1.01	0	0
155.5	4.223	4.221	0.002	0.31	0.31	0	0.002	3.087	3.089	-0.002	1.05	1.05	-0.002	0.003
154.1	4.247	4.247	0	0.29	0.29	0	0	3.096	3.096	0	1.09	1.09	0	0
152.6	4.273	4.272	0	0.27	0.27	0	0	3.105	3.105	0	1.14	1.14	0	0
151.1	4.298	4.298	0	0.25	0.25	0	0	3.116	3.116	0	1.19	1.19	0	0
149.6	4.323	4.323	0	0.23	0.23	0	0	3.131	3.131	0	1.24	1.24	0	0.001
148.1	4.349	4.348	0.001	0.21	0.21	0	0.001	3.149	3.15	-0.001	1.3	1.3	0	0.001
146.7	4.373	4.373	-0.001	0.19	0.19	0	0.001	3.174	3.173	0.001	1.35	1.35	0.001	0.001
145.1	4.4	4.399	0.001	0.17	0.17	0	0.001	3.2	3.201	-0.001	1.41	1.41	-0.001	0.001
143.7	4.423	4.424	-0.001	0.14	0.14	0	0.001	3.238	3.237	0.001	1.48	1.47	0	0.001
142.2	4.449	4.449	0	0.12	0.12	0	0	3.283	3.282	0	1.54	1.54	0	0
140.7	4.474	4.475	0	0.1	0.1	0	0	3.34	3.34	0	1.61	1.61	0	0
139.2	4.5	4.5	0	0.08	0.08	0	0	3.417	3.416	0	1.68	1.68	0	0
137.7	4.525	4.526	0	0.06	0.06	0	0	3.524	3.523	0.001	1.76	1.76	0	0.001
136.2	4.551	4.551	-0.001	0.04	0.04	0	0.001	3.688	3.687	0.001	1.85	1.85	0	0.001
134.7	4.576	4.577	-0.001	0.02	0.02	0	0.001	4.001	4	0.001	1.94	1.94	0	0.001
133.2	4.602	4.603	-0.002	0	0	0	0.002	0	0	0	0	0	0	0
131.6	4.629	4.629	0	-0.02	-0.02	0	0	0	0	0	0	0	0	0
130	4.656	4.655	0	-0.05	-0.05	0	0	0	0	0	0	0	0	0
128.5	4.681	4.682	-0.001	-0.07	-0.07	0	0.001	0	0	0	0	0	0	0
126.9	4.708	4.708	0	-0.09	-0.09	0	0	0	0	0	0	0	0	0
125.3	4.735	4.735	0	-0.11	-0.11	0	0	0	0	0	0	0	0	0
123.7	4.763	4.763	0	-0.13	-0.13	0	0	0	0	0	0	0	0	0
122.1	4.79	4.79	0	-0.15	-0.15	0	0	0	0	0	0	0	0	0
120.4	4.819	4.818	0.001	-0.17	-0.17	0	0.001	0	0	0	0	0	0	0
118.7	4.847	4.846	0.002	-0.19	-0.19	0	0.002	0	0	0	0	0	0	0
117.1	4.875	4.874	0.001	-0.22	-0.22	0	0.001	0	0	0	0	0	0	0
115.3	4.905	4.903	0.002	-0.24	-0.24	0	0.002	0	0	0	0	0	0	0
113.6	4.934	4.932	0.002	-0.26	-0.26	0	0.002	0	0	0	0	0	0	0
111.9	4.963	4.961	0.001	-0.28	-0.28	0	0.001	0	0	0	0	0	0	0
110.2	4.992	4.991	0	-0.3	-0.3	0	0	0	0	0	0	0	0	0
108.5	5.02	5.021	-0.001	-0.32	-0.32	0	0.001	0	0	0	0	0	0	0
106.7	5.051	5.052	-0.001	-0.34	-0.34	0	0.001	0	0	0	0	0	0	0
104.9	5.081	5.083	-0.002	-0.36	-0.36	0	0.002	0	0	0	0	0	0	0

AVERAGE SUM SQUARES

OF	RESID	1	7.3E-07	1	7.4E-08	1.9E-06	2	3.8E-07	1	5.6E-07	4.0E-06
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NUMBER OF TITRATIONS = 1

TOTAL BER OF TITRATIONS = 79

Appendix 11: Determination of Cr^{III}-Bpy stability constants (-CrOH) L_T:M_T ratio 3

TASK ZBAR BYP0 COMPLS WITH Cr(III) ratio 3 bis

MODL Cr+3 BYP0 H +1

CPLX 0 0 -13 800 H (-1)

CPLX 0 0 4.920 B\ (1) H +1(1)

CPLX 1 0 2.400 Cr(1) BY0(1)

CPLX 1 0 4.000 Cr(1) BY0(2)

CPLX 1 0 7.810 Cr(1) BY0(3)

CPLX 1 0 -1 790 Cr(1) BY0(1) H +1(-)

CPLX 1 0 -7 160 Cr(1) BY0(1) H +1(- :)

CONC

VESL IVOL 0.000 (0

VESL H +1 (116744 0

VESL Cr+3 (024920 0

VESL BYP0 076685 0

BUR1 H +1 -1217250 0

ELEC

ZERO H +1 4.26 0

GRAD H +1 8.859 0

DATA

0 EMF		PH		ZBAR(H)			POINT		PA			ZBAR(IM)			POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID		
263.9	2.385	2.384	0.001	0.98	0.98	0.001	0.001	4.229	4.23	-0.001	0.02	0.03	-0.002	0.003		
263.1	2.398	2.397	0.001	0.98	0.98	0.001	0.001	4.218	4.219	-0.001	0.02	0.03	-0.003	0.003		
262.3	2.412	2.411	0.001	0.98	0.98	0.001	0.001	4.207	4.208	-0.001	0.02	0.03	-0.003	0.003		
261.6	2.424	2.425	-0.001	0.98	0.98	-0.001	0.002	4.198	4.196	0.002	0.03	0.03	0.004	0.005		
260.8	2.437	2.439	-0.002	0.98	0.98	-0.002	0.003	4.187	4.185	0.003	0.04	0.03	0.006	0.007		
259.9	2.453	2.454	-0.001	0.98	0.98	-0.001	0.002	4.174	4.173	0.002	0.03	0.03	0.004	0.004		
259	2.468	2.469	-0.001	0.98	0.98	-0.001	0.001	4.161	4.16	0.001	0.03	0.03	0.002	0.002		
258.2	2.482	2.484	-0.002	0.98	0.98	-0.002	0.003	4.15	4.147	0.003	0.04	0.03	0.007	0.008		
257.2	2.499	2.499	-0.001	0.98	0.98	-0.001	0.001	4.135	4.134	0.001	0.03	0.03	0.002	0.002		
256.3	2.514	2.515	-0.001	0.98	0.98	-0.001	0.002	4.123	4.121	0.002	0.04	0.03	0.004	0.004		
255.4	2.529	2.531	-0.002	0.98	0.98	-0.002	0.003	4.11	4.107	0.003	0.04	0.03	0.007	0.008		
254.4	2.546	2.548	-0.002	0.98	0.98	-0.002	0.003	4.095	4.092	0.003	0.04	0.04	0.006	0.007		
253.4	2.563	2.565	-0.002	0.97	0.98	-0.002	0.003	4.081	4.078	0.003	0.04	0.04	0.006	0.007		
252.4	2.58	2.583	-0.003	0.97	0.98	-0.002	0.004	4.066	4.063	0.004	0.05	0.04	0.008	0.009		
251.3	2.599	2.601	-0.002	0.97	0.97	-0.002	0.003	4.05	4.047	0.003	0.05	0.04	0.006	0.007		
250.3	2.616	2.62	-0.004	0.97	0.97	-0.003	0.005	4.036	4.031	0.005	0.05	0.04	0.01	0.011		
249.1	2.636	2.639	-0.003	0.97	0.97	-0.002	0.003	4.018	4.014	0.004	0.05	0.04	0.007	0.007		
248	2.655	2.659	-0.004	0.97	0.97	-0.003	0.005	4.002	3.997	0.005	0.05	0.05	0.009	0.01		
246.8	2.675	2.679	-0.004	0.97	0.97	-0.003	0.005	3.984	3.979	0.005	0.06	0.05	0.008	0.01		
245.6	2.696	2.7	-0.004	0.97	0.97	-0.003	0.005	3.966	3.961	0.006	0.06	0.05	0.009	0.011		
244.3	2.718	2.722	-0.004	0.96	0.97	-0.002	0.005	3.947	3.942	0.005	0.06	0.05	0.008	0.01		
243	2.74	2.744	-0.004	0.96	0.97	-0.003	0.005	3.927	3.922	0.005	0.06	0.05	0.009	0.01		
241.7	2.762	2.767	-0.005	0.96	0.96	-0.003	0.006	3.908	3.902	0.007	0.07	0.06	0.01	0.012		
240.2	2.787	2.791	-0.004	0.96	0.96	-0.002	0.004	3.885	3.881	0.005	0.07	0.06	0.007	0.008		
238.8	2.811	2.816	-0.005	0.96	0.96	-0.002	0.005	3.865	3.859	0.006	0.07	0.06	0.008	0.01		
237.2	2.838	2.841	-0.003	0.96	0.96	-0.002	0.003	3.84	3.836	0.004	0.07	0.07	0.005	0.007		
235.7	2.864	2.868	-0.004	0.95	0.95	-0.002	0.005	3.818	3.813	0.005	0.08	0.07	0.007	0.008		
234	2.893	2.895	-0.003	0.95	0.95	-0.001	0.003	3.792	3.789	0.003	0.08	0.07	0.004	0.005		
232.3	2.922	2.924	-0.002	0.95	0.95	-0.001	0.002	3.766	3.764	0.002	0.08	0.08	0.003	0.004		
230.6	2.95	2.953	-0.002	0.94	0.95	-0.001	0.002	3.741	3.738	0.003	0.09	0.08	0.003	0.004		
228.8	2.981	2.983	-0.002	0.94	0.94	-0.001	0.002	3.713	3.712	0.002	0.09	0.09	0.002	0.003		
226.9	3.013	3.014	0	0.94	0.94	0	0	3.685	3.684	0	0.1	0.1	0	0.001		

225.1	3.044	3.045	-0.001	0.93	0.93	0	0.002	3.658	3.657	0.002	0.11	0.1	0.002	0.002
223.1	3.078	3.078	0	0.93	0.93	0	0	3.628	3.628	0	0.11	0.11	0	0
221.2	3.11	3.111	-0.001	0.92	0.92	0	0.001	3.6	3.6	0.001	0.12	0.12	0.001	0.001
219.1	3.146	3.144	0.001	0.92	0.92	0	0.001	3.569	3.571	-0.002	0.13	0.13	-0.002	0.002
217.1	3.18	3.178	0.001	0.91	0.91	0	0.001	3.54	3.542	-0.002	0.14	0.14	-0.002	0.002
215	3.215	3.213	0.003	0.9	0.9	0.001	0.003	3.509	3.513	-0.003	0.15	0.15	-0.003	0.004
213	3.249	3.247	0.003	0.9	0.9	0.001	0.003	3.481	3.484	-0.003	0.16	0.16	-0.003	0.004
211	3.283	3.281	0.002	0.89	0.89	0	0.003	3.452	3.455	-0.003	0.17	0.18	-0.002	0.004
208.9	3.319	3.315	0.004	0.88	0.88	0.001	0.004	3.423	3.427	-0.005	0.19	0.19	-0.004	0.006
206.9	3.353	3.348	0.005	0.87	0.87	0.001	0.005	3.395	3.4	-0.005	0.2	0.2	-0.005	0.007
205	3.385	3.381	0.004	0.86	0.86	0.001	0.004	3.369	3.373	-0.004	0.22	0.22	-0.004	0.006
203.1	3.418	3.414	0.004	0.85	0.85	0.001	0.004	3.343	3.347	-0.004	0.23	0.24	-0.004	0.005
201.2	3.45	3.446	0.004	0.84	0.84	0.001	0.004	3.318	3.323	-0.004	0.25	0.25	-0.004	0.006
199.4	3.481	3.477	0.004	0.83	0.83	0	0.004	3.295	3.299	-0.004	0.27	0.27	-0.004	0.005
197.7	3.509	3.507	0.002	0.82	0.82	0	0.002	3.273	3.276	-0.002	0.29	0.29	-0.002	0.003
195.9	3.54	3.537	0.003	0.81	0.81	0	0.003	3.25	3.254	-0.003	0.31	0.31	-0.003	0.005
194.2	3.569	3.566	0.003	0.8	0.8	0	0.003	3.229	3.233	-0.003	0.33	0.33	-0.003	0.005
192.7	3.594	3.594	0	0.79	0.79	0	0	3.212	3.213	-0.001	0.35	0.35	-0.001	0.001
191.1	3.622	3.621	0	0.78	0.78	0	0	3.193	3.194	0	0.37	0.37	0	0
189.6	3.647	3.648	-0.001	0.76	0.76	0	0.001	3.176	3.175	0.001	0.39	0.39	0.001	0.002
188.1	3.673	3.674	-0.002	0.75	0.75	0	0.002	3.16	3.158	0.002	0.42	0.41	0.002	0.003
186.6	3.698	3.7	-0.002	0.74	0.74	0	0.002	3.143	3.141	0.002	0.44	0.44	0.002	0.003
185.2	3.722	3.725	-0.003	0.73	0.73	0	0.003	3.128	3.125	0.003	0.46	0.46	0.003	0.004
183.7	3.747	3.749	-0.002	0.71	0.71	0	0.002	3.112	3.11	0.002	0.49	0.48	0.002	0.003
182.4	3.769	3.773	-0.003	0.7	0.7	0	0.003	3.1	3.096	0.004	0.51	0.51	0.004	0.005
181	3.793	3.796	-0.003	0.69	0.69	0	0.003	3.085	3.082	0.003	0.54	0.53	0.004	0.005
179.7	3.815	3.819	-0.004	0.68	0.68	0	0.004	3.073	3.069	0.004	0.56	0.56	0.005	0.006
178.4	3.837	3.842	-0.004	0.66	0.66	0	0.004	3.061	3.057	0.005	0.59	0.58	0.005	0.007
177.1	3.859	3.864	-0.004	0.65	0.65	0	0.004	3.05	3.045	0.005	0.61	0.61	0.006	0.007
175.8	3.881	3.886	-0.004	0.64	0.64	0	0.004	3.038	3.034	0.004	0.64	0.64	0.005	0.007
174.5	3.904	3.907	-0.003	0.62	0.62	0	0.003	3.027	3.023	0.004	0.67	0.66	0.005	0.006
173.2	3.926	3.928	-0.003	0.61	0.61	0	0.003	3.015	3.013	0.003	0.69	0.69	0.003	0.004
172	3.946	3.949	-0.003	0.6	0.6	0	0.003	3.006	3.003	0.003	0.72	0.72	0.004	0.005
170.7	3.968	3.97	-0.002	0.58	0.58	0	0.002	2.996	2.994	0.002	0.75	0.74	0.002	0.003
169.5	3.989	3.99	-0.002	0.57	0.57	0	0.002	2.987	2.985	0.002	0.77	0.77	0.002	0.003
168.3	4.009	4.01	-0.001	0.56	0.56	0	0.001	2.979	2.977	0.001	0.8	0.8	0.002	0.002
167.1	4.029	4.03	-0.001	0.54	0.54	0	0.001	2.97	2.969	0.001	0.83	0.83	0.001	0.002
165.9	4.05	4.05	0	0.53	0.53	0	0	2.963	2.962	0	0.86	0.86	0.001	0.001
164.7	4.07	4.07	0	0.52	0.52	0	0	2.955	2.955	0	0.89	0.89	0	0.001
163.5	4.09	4.089	0.001	0.5	0.5	0	0.001	2.948	2.949	-0.001	0.92	0.92	-0.002	0.002
162.4	4.109	4.109	0	0.49	0.49	0	0	2.943	2.943	0	0.95	0.95	-0.001	0.001
161.2	4.13	4.128	0.002	0.48	0.48	0	0.002	2.936	2.938	-0.002	0.98	0.98	-0.003	0.003
160	4.15	4.147	0.003	0.46	0.46	0	0.003	2.93	2.933	-0.003	1.01	1.02	-0.004	0.005
159	4.167	4.166	0.001	0.45	0.45	0	0.001	2.928	2.928	-0.001	1.05	1.05	-0.001	0.001
157.8	4.187	4.185	0.002	0.43	0.43	0	0.002	2.922	2.924	-0.002	1.08	1.08	-0.003	0.004
156.7	4.206	4.204	0.002	0.42	0.42	0	0.002	2.919	2.921	-0.002	1.11	1.12	-0.003	0.004
155.5	4.226	4.223	0.003	0.41	0.41	0	0.003	2.915	2.918	-0.003	1.15	1.15	-0.006	0.006
154.5	4.243	4.242	0.001	0.39	0.39	0	0.001	2.914	2.916	-0.001	1.19	1.19	-0.002	0.003
153.3	4.264	4.261	0.003	0.38	0.38	0	0.003	2.911	2.914	-0.003	1.22	1.23	-0.005	0.006
152.2	4.282	4.28	0.003	0.37	0.37	0	0.003	2.91	2.913	-0.003	1.26	1.26	-0.005	0.006
151.1	4.301	4.298	0.003	0.35	0.35	0	0.003	2.909	2.912	-0.003	1.3	1.3	-0.005	0.006
150	4.32	4.317	0.003	0.34	0.34	0	0.003	2.91	2.912	-0.003	1.34	1.34	-0.005	0.006
148.9	4.339	4.336	0.003	0.32	0.32	0	0.003	2.91	2.913	-0.003	1.38	1.38	-0.005	0.005
147.9	4.355	4.355	0.001	0.31	0.31	0	0.001	2.914	2.915	-0.001	1.43	1.43	-0.002	0.002
146.7	4.376	4.373	0.003	0.3	0.3	0	0.003	2.915	2.918	-0.003	1.47	1.47	-0.004	0.005
145.7	4.393	4.392	0.001	0.28	0.28	0	0.001	2.92	2.921	-0.001	1.52	1.52	-0.001	0.001

144.5	4.413	4.411	0.002	0.27	0.27	0	0.002	2.923	2.926	-0.002	1.56	1.57	-0.004	0.005
143.5	4.43	4.43	0	0.25	0.25	0	0	2.931	2.931	0	1.61	1.61	-0.001	0.001
142.4	4.449	4.449	0	0.24	0.24	0	0	2.938	2.938	0	1.67	1.67	0	0
141.3	4.468	4.468	0	0.23	0.23	0	0	2.947	2.947	0	1.72	1.72	0	0
140.2	4.486	4.487	0	0.21	0.21	0	0	2.957	2.957	0	1.77	1.77	0	0.001
139	4.507	4.506	0.001	0.2	0.2	0	0.001	2.967	2.968	-0.001	1.83	1.83	-0.002	0.002
137.9	4.525	4.525	0.001	0.19	0.19	0	0.001	2.982	2.982	-0.001	1.89	1.89	-0.001	0.001
136.8	4.544	4.544	0	0.17	0.17	0	0	2.998	2.999	0	1.96	1.96	0	0
135.7	4.563	4.563	0	0.16	0.16	0	0	3.018	3.018	0	2.02	2.02	0	0.001
134.6	4.581	4.582	-0.001	0.14	0.14	0	0.001	3.041	3.04	0.001	2.09	2.09	0.001	0.002
133.5	4.6	4.602	-0.002	0.13	0.13	0	0.002	3.069	3.067	0.002	2.17	2.17	0.002	0.003
132.3	4.621	4.621	-0.001	0.12	0.12	0	0.001	3.099	3.099	0.001	2.24	2.24	0.001	0.001
131.2	4.639	4.641	-0.001	0.1	0.1	0	0.001	3.138	3.137	0.002	2.33	2.33	0.002	0.002
130	4.66	4.66	-0.001	0.09	0.09	0	0.001	3.184	3.183	0.001	2.41	2.41	0.001	0.001
128.9	4.678	4.68	-0.002	0.07	0.07	0	0.002	3.242	3.24	0.002	2.5	2.5	0.001	0.002
127.7	4.699	4.7	-0.001	0.06	0.06	0	0.001	3.315	3.314	0.001	2.6	2.6	0.001	0.001
126.6	4.717	4.72	-0.002	0.05	0.05	0	0.002	3.415	3.412	0.002	2.7	2.7	0.001	0.003
125.4	4.738	4.74	-0.002	0.03	0.03	0	0.002	3.556	3.554	0.002	2.81	2.81	0.001	0.002
124.2	4.758	4.76	-0.002	0.02	0.02	0	0.002	3.793	3.791	0.002	2.92	2.92	0	0.002
123	4.779	4.78	-0.001	0	0	0	0.001	4.485	4.482	0.003	3.05	3.05	0	0.003
121.8	4.799	4.8	-0.001	-0.01	-0.01	0	0.001	0	0	0	0	0	0	0
120.6	4.819	4.821	-0.001	-0.02	-0.02	0	0.001	0	0	0	0	0	0	0
119.3	4.841	4.841	0	-0.04	-0.04	0	0	0	0	0	0	0	0	0
118.1	4.862	4.862	0	-0.05	-0.05	0	0	0	0	0	0	0	0	0
116.9	4.882	4.883	-0.001	-0.07	-0.07	0	0.001	0	0	0	0	0	0	0
115.6	4.904	4.904	0.001	-0.08	-0.08	0	0.001	0	0	0	0	0	0	0
114.3	4.926	4.925	0.001	-0.09	-0.09	0	0.001	0	0	0	0	0	0	0
113.1	4.947	4.946	0.001	-0.11	-0.11	0	0.001	0	0	0	0	0	0	0
111.8	4.969	4.968	0.001	-0.12	-0.12	0	0.001	0	0	0	0	0	0	0
110.5	4.991	4.989	0.002	-0.14	-0.14	0	0.002	0	0	0	0	0	0	0
109.2	5.013	5.011	0.002	-0.15	-0.15	0	0.002	0	0	0	0	0	0	0
107.9	5.035	5.033	0.002	-0.17	-0.17	0	0.002	0	0	0	0	0	0	0

AVERAGE SUM SQUARES

OF	RESIDUAL	5	6.8E-05	9	9.2E-06	6.7E-06	8	2.2E-07	1	7.5E-06	2.6E-05
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NUMBER OF TITRATIONS = 1

TOTAL BERBERONS = 20

Appendix 12: Determination of Cr^{III}-Bpy stability constants (-CrOH) L_T:M_T ratio 4

TASK ZBAR BYP 0 COMIES WITCr(III) ratio 4

MODL Cr+3 BYP0 F 1

CPLX 0 0 -13800 H 1(-1)

CPLX 0 0 4.920 BY0(1) H +1(1)

CPLX 1 0 2.340 Cr 3(1) B P0(1)

CPLX 1 0 5.420 Cr 3(1) B P0(2)

CPLX 1 0 -1.590 Cr 3(1) B P0(1) H +1(- 1)

CPLX 1 0 -6.700 Cr 3(1) B P0(1) H +1(- 2)

CPLX 1 0 -13500 Cr 3(1) B P0(1) H +1(- 3)

CONC

VESL IVOL 0.000 (0

VESL H +1 (1E+05 0 0

VESL Cr+3 (18150 0 0

VESL BYP0 81798 0 0

BUR1 H +1 -(2E+05 0 0

ELEC

ZERO H +1 5.02 0

GRAD H +1 8.66 0

DATA

0 EMF		PH		ZBAR(F H)			POINT		PA			ZBAR(M M)		POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID	
244.1	2.743	2.75	-0.006	0.97	0.97	-0.003	0.007	3.88	3.873	0.008	0.05	0.04	0.017	0.019	
242.7	2.767	2.773	-0.006	0.97	0.97	-0.003	0.006	3.859	3.852	0.007	0.05	0.04	0.014	0.016	
241.3	2.791	2.797	-0.006	0.97	0.97	-0.003	0.006	3.838	3.831	0.007	0.06	0.04	0.014	0.015	
239.8	2.817	2.821	-0.005	0.97	0.97	-0.002	0.005	3.815	3.809	0.006	0.06	0.05	0.011	0.013	
238.3	2.842	2.847	-0.005	0.97	0.97	-0.002	0.005	3.792	3.786	0.006	0.06	0.05	0.011	0.012	
236.7	2.869	2.873	-0.004	0.96	0.97	-0.002	0.004	3.767	3.763	0.005	0.06	0.05	0.009	0.01	
235.1	2.897	2.901	-0.004	0.96	0.96	-0.002	0.004	3.743	3.738	0.005	0.06	0.06	0.008	0.01	
233.4	2.926	2.929	-0.003	0.96	0.96	-0.001	0.004	3.717	3.713	0.004	0.07	0.06	0.007	0.008	
231.6	2.956	2.958	-0.002	0.96	0.96	-0.001	0.002	3.689	3.687	0.002	0.07	0.07	0.004	0.004	
229.9	2.985	2.988	-0.003	0.95	0.95	-0.001	0.003	3.664	3.661	0.003	0.08	0.07	0.005	0.006	
228	3.018	3.019	-0.001	0.95	0.95	0	0.001	3.635	3.633	0.002	0.08	0.08	0.002	0.003	
226.1	3.05	3.051	-0.001	0.95	0.95	0	0.001	3.606	3.605	0.001	0.09	0.08	0.001	0.001	
224.2	3.083	3.083	-0.001	0.94	0.94	0	0.001	3.577	3.577	0.001	0.09	0.09	0.001	0.001	
222.2	3.117	3.116	0.001	0.94	0.94	0	0.001	3.547	3.548	-0.001	0.1	0.1	-0.001	0.001	
220.2	3.151	3.149	0.001	0.93	0.93	0	0.001	3.517	3.519	-0.002	0.11	0.11	-0.002	0.003	
218.2	3.185	3.183	0.002	0.93	0.93	0	0.002	3.488	3.49	-0.002	0.12	0.12	-0.003	0.004	
216.2	3.219	3.217	0.002	0.92	0.92	0	0.002	3.458	3.461	-0.003	0.13	0.13	-0.003	0.004	
214.2	3.253	3.25	0.003	0.92	0.91	0.001	0.003	3.429	3.432	-0.003	0.14	0.15	-0.004	0.005	
212.2	3.287	3.284	0.004	0.91	0.91	0.001	0.004	3.4	3.404	-0.004	0.16	0.16	-0.005	0.006	
210.2	3.321	3.317	0.005	0.9	0.9	0.001	0.005	3.371	3.376	-0.005	0.17	0.18	-0.006	0.008	
208.3	3.354	3.349	0.004	0.89	0.89	0.001	0.004	3.345	3.349	-0.005	0.19	0.19	-0.006	0.008	
206.4	3.386	3.381	0.005	0.88	0.88	0.001	0.005	3.318	3.323	-0.005	0.21	0.21	-0.007	0.008	
204.6	3.417	3.412	0.004	0.88	0.88	0.001	0.004	3.294	3.298	-0.004	0.23	0.23	-0.006	0.007	
202.8	3.447	3.443	0.004	0.87	0.87	0.001	0.004	3.269	3.274	-0.005	0.25	0.25	-0.006	0.007	
201	3.478	3.473	0.005	0.86	0.86	0.001	0.005	3.245	3.25	-0.005	0.27	0.27	-0.007	0.009	
199.4	3.505	3.502	0.003	0.85	0.85	0	0.003	3.225	3.228	-0.003	0.29	0.29	-0.005	0.006	
197.8	3.533	3.53	0.002	0.84	0.84	0	0.002	3.204	3.207	-0.002	0.31	0.32	-0.003	0.004	
196.2	3.56	3.558	0.002	0.83	0.83	0	0.002	3.184	3.186	-0.002	0.34	0.34	-0.003	0.003	
194.7	3.585	3.585	0	0.82	0.82	0	0	3.166	3.166	0	0.36	0.36	-0.001	0.001	
193.1	3.613	3.611	0.001	0.81	0.81	0	0.001	3.146	3.147	-0.002	0.39	0.39	-0.002	0.003	
191.7	3.637	3.637	0	0.8	0.8	0	0	3.13	3.129	0	0.42	0.41	0	0.001	
190.3	3.66	3.662	-0.001	0.79	0.79	0	0.001	3.113	3.112	0.001	0.44	0.44	0.002	0.003	

188.8	3.686	3.686	0	0.78	0.78	0	0	3.096	3.095	0	0.47	0.47	0	0.001
187.6	3.706	3.71	-0.004	0.76	0.76	0	0.004	3.083	3.079	0.004	0.5	0.49	0.006	0.007
186.2	3.73	3.733	-0.003	0.75	0.75	0	0.003	3.067	3.064	0.003	0.53	0.52	0.005	0.006
184.9	3.752	3.756	-0.004	0.74	0.74	0	0.004	3.054	3.05	0.004	0.56	0.55	0.007	0.008
183.6	3.775	3.779	-0.004	0.73	0.73	0	0.004	3.04	3.035	0.004	0.58	0.58	0.007	0.009
182.3	3.797	3.801	-0.004	0.72	0.72	0	0.004	3.026	3.022	0.004	0.61	0.61	0.007	0.009
181.1	3.817	3.823	-0.005	0.71	0.71	0	0.005	3.014	3.009	0.005	0.64	0.63	0.01	0.011
179.8	3.839	3.844	-0.004	0.7	0.7	0	0.004	3.001	2.997	0.005	0.67	0.66	0.008	0.01
178.6	3.86	3.865	-0.005	0.68	0.68	0	0.005	2.99	2.985	0.005	0.7	0.69	0.01	0.011
177.4	3.88	3.885	-0.005	0.67	0.67	0	0.005	2.978	2.973	0.005	0.73	0.72	0.01	0.011
176.2	3.901	3.906	-0.005	0.66	0.66	0	0.005	2.967	2.962	0.005	0.76	0.75	0.01	0.011
174.9	3.923	3.926	-0.003	0.65	0.65	0	0.003	2.954	2.951	0.003	0.79	0.78	0.006	0.007
173.8	3.942	3.946	-0.004	0.64	0.64	0	0.004	2.945	2.941	0.004	0.82	0.82	0.009	0.01
172.6	3.962	3.965	-0.003	0.63	0.63	0	0.003	2.935	2.931	0.003	0.85	0.85	0.007	0.008
171.4	3.983	3.985	-0.002	0.61	0.61	0	0.002	2.924	2.922	0.002	0.88	0.88	0.005	0.006
170.3	4.001	4.004	-0.003	0.6	0.6	0	0.003	2.916	2.913	0.003	0.92	0.91	0.006	0.007
169.1	4.022	4.023	-0.001	0.59	0.59	0	0.001	2.905	2.904	0.002	0.95	0.94	0.003	0.004
167.9	4.042	4.042	0	0.58	0.58	0	0	2.895	2.896	0	0.98	0.98	0	0
166.8	4.061	4.061	0	0.57	0.57	0	0	2.887	2.887	0	1.01	1.01	0	0
165.7	4.08	4.08	0	0.55	0.55	0	0	2.88	2.88	0	1.04	1.04	0	0
164.5	4.1	4.098	0.002	0.54	0.54	0	0.002	2.87	2.872	-0.002	1.07	1.08	-0.005	0.006
163.5	4.117	4.117	0.001	0.53	0.53	0	0.001	2.865	2.865	-0.001	1.11	1.11	-0.002	0.002
162.4	4.136	4.135	0.001	0.52	0.52	0	0.001	2.858	2.859	-0.001	1.14	1.15	-0.003	0.003
161.2	4.156	4.153	0.003	0.51	0.51	0	0.003	2.849	2.852	-0.003	1.17	1.18	-0.009	0.009
160.2	4.174	4.171	0.002	0.49	0.49	0	0.002	2.844	2.846	-0.002	1.21	1.22	-0.006	0.006
159.1	4.192	4.189	0.003	0.48	0.48	0	0.003	2.838	2.841	-0.003	1.25	1.25	-0.008	0.008
158	4.211	4.207	0.004	0.47	0.47	0	0.004	2.832	2.835	-0.004	1.28	1.29	-0.01	0.011
157	4.228	4.225	0.003	0.46	0.46	0	0.003	2.828	2.83	-0.003	1.32	1.33	-0.007	0.008
155.9	4.247	4.243	0.004	0.45	0.45	0	0.004	2.822	2.826	-0.004	1.36	1.37	-0.01	0.011
154.8	4.266	4.261	0.004	0.43	0.43	0	0.004	2.817	2.821	-0.005	1.4	1.41	-0.012	0.013
153.8	4.283	4.279	0.004	0.42	0.42	0	0.004	2.814	2.818	-0.004	1.44	1.45	-0.01	0.011
152.8	4.3	4.297	0.003	0.41	0.41	0	0.003	2.811	2.814	-0.003	1.48	1.49	-0.008	0.009
151.7	4.318	4.315	0.004	0.4	0.4	0	0.004	2.807	2.811	-0.004	1.52	1.53	-0.011	0.011
150.7	4.335	4.333	0.003	0.38	0.38	0	0.003	2.805	2.808	-0.003	1.57	1.58	-0.009	0.009
149.7	4.353	4.35	0.002	0.37	0.37	0	0.002	2.804	2.806	-0.002	1.62	1.62	-0.006	0.007
148.6	4.371	4.368	0.003	0.36	0.36	0	0.003	2.801	2.804	-0.003	1.66	1.67	-0.009	0.01
147.6	4.388	4.386	0.002	0.35	0.35	0	0.002	2.801	2.803	-0.002	1.71	1.72	-0.007	0.007
146.6	4.405	4.404	0.001	0.33	0.33	0	0.001	2.801	2.803	-0.001	1.76	1.76	-0.004	0.004
145.5	4.424	4.422	0.002	0.32	0.32	0	0.002	2.8	2.802	-0.002	1.81	1.82	-0.007	0.007
144.5	4.441	4.44	0.001	0.31	0.31	0	0.001	2.802	2.803	-0.001	1.86	1.87	-0.004	0.004
143.4	4.46	4.458	0.002	0.3	0.3	0	0.002	2.802	2.804	-0.002	1.92	1.92	-0.006	0.007
142.4	4.477	4.476	0.001	0.29	0.29	0	0.001	2.805	2.806	-0.001	1.97	1.98	-0.003	0.004
141.3	4.496	4.494	0.002	0.27	0.27	0	0.002	2.807	2.808	-0.002	2.03	2.04	-0.005	0.006
140.3	4.513	4.512	0.001	0.26	0.26	0	0.001	2.811	2.812	-0.001	2.1	2.1	-0.002	0.002
139.2	4.532	4.53	0.001	0.25	0.25	0	0.001	2.815	2.816	-0.001	2.16	2.16	-0.004	0.004
138.2	4.549	4.549	0	0.24	0.24	0	0	2.821	2.821	0	2.23	2.23	0	0
137.2	4.566	4.567	-0.001	0.22	0.22	0	0.001	2.829	2.828	0.001	2.3	2.3	0.004	0.004
136.1	4.584	4.585	-0.001	0.21	0.21	0	0.001	2.837	2.836	0.001	2.37	2.37	0.003	0.003
135	4.603	4.604	-0.001	0.2	0.2	0	0.001	2.845	2.845	0.001	2.45	2.45	0.002	0.002
133.9	4.622	4.623	-0.001	0.19	0.19	0	0.001	2.856	2.855	0.001	2.53	2.53	0.002	0.002
132.8	4.641	4.641	-0.001	0.17	0.17	0	0.001	2.869	2.868	0.001	2.61	2.61	0.002	0.002
131.7	4.659	4.66	-0.001	0.16	0.16	0	0.001	2.883	2.882	0.001	2.7	2.7	0.002	0.002
130.6	4.678	4.679	-0.001	0.15	0.15	0	0.001	2.9	2.899	0.001	2.8	2.79	0.003	0.003
129.5	4.697	4.698	-0.001	0.14	0.14	0	0.001	2.921	2.919	0.001	2.9	2.89	0.003	0.004
128.4	4.716	4.718	-0.002	0.12	0.12	0	0.002	2.945	2.943	0.002	3	3	0.004	0.005
127.2	4.736	4.737	-0.001	0.11	0.11	0	0.001	2.971	2.97	0.001	3.11	3.11	0.002	0.002

126.1	4.755	4.757	-0.002	0.1	0.1	0	0.002	3.004	3.003	0.002	3.23	3.23	0.003	0.004
124.9	4.775	4.776	-0.001	0.09	0.09	0	0.001	3.043	3.042	0.001	3.35	3.35	0.002	0.002
123.8	4.794	4.796	-0.002	0.08	0.08	0	0.002	3.092	3.09	0.002	3.49	3.48	0.003	0.004
122.6	4.815	4.816	-0.002	0.06	0.06	0	0.002	3.151	3.15	0.002	3.63	3.63	0.002	0.003
121.4	4.835	4.836	-0.001	0.05	0.05	0	0.001	3.228	3.226	0.002	3.78	3.78	0.002	0.002
120.2	4.855	4.857	-0.001	0.04	0.04	0	0.001	3.332	3.33	0.001	3.94	3.94	0.001	0.002
119	4.876	4.877	-0.002	0.03	0.03	0	0.002	3.485	3.484	0.002	4.11	4.11	0.001	0.002
117.7	4.898	4.898	0	0.01	0.01	0	0	3.755	3.754	0	4.3	4.3	0	0
116.6	4.917	4.919	-0.003	0	0	0	0.003	5.052	5.04	0.012	4.5	4.5	0	0.012
115.3	4.939	4.941	-0.002	-0.01	-0.01	0	0.002	0	0	0	0	0	0	0
114	4.961	4.962	-0.001	-0.02	-0.02	0	0.001	0	0	0	0	0	0	0
112.7	4.983	4.984	-0.001	-0.04	-0.04	0	0.001	0	0	0	0	0	0	0
111.4	5.005	5.006	-0.001	-0.05	-0.05	0	0.001	0	0	0	0	0	0	0
110.1	5.028	5.028	-0.001	-0.06	-0.06	0	0.001	0	0	0	0	0	0	0
108.8	5.05	5.051	-0.001	-0.07	-0.07	0	0.001	0	0	0	0	0	0	0
107.5	5.072	5.074	-0.002	-0.09	-0.09	0	0.002	0	0	0	0	0	0	0
106.1	5.096	5.097	-0.001	-0.1	-0.1	0	0.001	0	0	0	0	0	0	0
104.7	5.12	5.12	-0.001	-0.11	-0.11	0	0.001	0	0	0	0	0	0	0
103.3	5.144	5.144	-0.001	-0.12	-0.12	0	0.001	0	0	0	0	0	0	0
101.9	5.167	5.168	-0.001	-0.14	-0.14	0	0.001	0	0	0	0	0	0	0
100.4	5.193	5.193	0	-0.15	-0.15	0	0	0	0	0	0	0	0	0
98.9	5.219	5.218	0.001	-0.16	-0.16	0	0.001	0	0	0	0	0	0	0
97.4	5.244	5.243	0.001	-0.17	-0.17	0	0.001	0	0	0	0	0	0	0
95.9	5.27	5.269	0.001	-0.19	-0.19	0	0.001	0	0	0	0	0	0	0
94.3	5.297	5.295	0.002	-0.2	-0.2	0	0.002	0	0	0	0	0	0	0
92.7	5.324	5.322	0.002	-0.21	-0.21	0	0.002	0	0	0	0	0	0	0
91.1	5.352	5.349	0.003	-0.22	-0.22	0	0.003	0	0	0	0	0	0	0
89.4	5.38	5.376	0.004	-0.24	-0.24	0	0.004	0	0	0	0	0	0	0
87.8	5.408	5.405	0.003	-0.25	-0.25	0	0.003	0	0	0	0	0	0	0
86	5.438	5.433	0.005	-0.26	-0.26	0	0.005	0	0	0	0	0	0	0
84.3	5.467	5.462	0.005	-0.27	-0.27	0	0.005	0	0	0	0	0	0	0
82.7	5.495	5.492	0.003	-0.29	-0.29	0	0.003	0	0	0	0	0	0	0
81.2	5.52	5.522	-0.002	-0.3	-0.3	0	0.002	0	0	0	0	0	0	0
79.9	5.542	5.553	-0.011	-0.31	-0.31	0	0.011	0	0	0	0	0	0	0

AVERA F SUM QUARES

OF	RESIDI	8	8.4E-07	4	7.0E-09	9.2E-06	1	1.5E-06	4	1.0E-07	5.2E-05
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NUMBE F TITRONS = 1

TOTAL BER OINTS = 122

Appendix 13: Determination of Cr^{III}-Bpy stability constants (-CrOH) L_T:M_T ratio 9

TASK ZBAR 'BYP 0 COMFES WIT Cr(III) ratio 9

MODL Cr+3 BYP0 H 1

CPLX 0 0 -13 800 H+1(-1)

CPLX 0 0 4.920 BY0(1) H+1(1)

CPLX 1 0 1.280 Cr 3(1) B' P0(1)

CPLX 1 0 5.790 Cr 3(1) B' P0(2)

CPLX 1 0 -1.480 Cr 3(1) B' P0(1) H+1(-1)

CPLX 1 0 -7.140 Cr 3(1) B' P0(1) H+1(-2)

CPLX 1 0 -14 300 Cr 3(1) B' P0(1) H+1(-3)

CONC

VESL IVOL 0.000 C 0

VESL H+1 C 1E+05 0 0

VESL Cr+3 C 10028 0 0

VESL BYP0 92023 0 0

BUR1 H+1 -C 2E+05 0 0

ELEC

ZERO H+1 5.49 0

GRAD H+1 8.801 0

DATA

0 EMF		PH		ZBAR(H)			POINT		PA			ZBAR(M)			POINT	
OBS	OBS	CALC	RESID	OBS	CALC	RESID	RESID	OBS	CALC	RESID	OBS	CALC	RESID	RESID		
239.7	2.82	2.82	0	0.98	0.98	0	0	3.738	3.738	0	0.03	0.03	0	0		
238.1	2.847	2.846	0	0.97	0.97	0	0	3.714	3.714	0	0.03	0.03	-0.001	0.001		
236.3	2.877	2.874	0.003	0.97	0.97	0.001	0.003	3.685	3.689	-0.003	0.02	0.03	-0.011	0.011		
234.5	2.908	2.904	0.004	0.97	0.97	0.001	0.005	3.658	3.663	-0.005	0.02	0.04	-0.016	0.017		
232.7	2.939	2.934	0.005	0.97	0.97	0.002	0.005	3.63	3.636	-0.006	0.02	0.04	-0.017	0.018		
230.9	2.969	2.965	0.004	0.97	0.97	0.001	0.005	3.603	3.608	-0.005	0.03	0.04	-0.015	0.016		
228.9	3.003	2.997	0.006	0.97	0.96	0.002	0.006	3.572	3.579	-0.007	0.03	0.05	-0.02	0.021		
227	3.035	3.03	0.005	0.96	0.96	0.001	0.006	3.543	3.549	-0.006	0.04	0.05	-0.017	0.018		
224.9	3.071	3.064	0.007	0.96	0.96	0.002	0.007	3.51	3.518	-0.008	0.04	0.06	-0.021	0.022		
222.9	3.105	3.099	0.006	0.96	0.95	0.001	0.006	3.48	3.487	-0.007	0.05	0.07	-0.018	0.019		
220.8	3.141	3.135	0.006	0.95	0.95	0.001	0.006	3.448	3.455	-0.007	0.06	0.08	-0.018	0.019		
218.8	3.175	3.171	0.004	0.95	0.95	0.001	0.004	3.419	3.423	-0.005	0.08	0.09	-0.012	0.013		
216.7	3.211	3.207	0.004	0.94	0.94	0.001	0.004	3.387	3.391	-0.004	0.09	0.1	-0.01	0.011		
214.5	3.248	3.243	0.005	0.94	0.93	0.001	0.005	3.354	3.36	-0.005	0.1	0.12	-0.013	0.014		
212.5	3.282	3.279	0.003	0.93	0.93	0	0.003	3.325	3.328	-0.003	0.13	0.13	-0.007	0.008		
210.4	3.318	3.315	0.003	0.92	0.92	0	0.003	3.295	3.298	-0.003	0.14	0.15	-0.007	0.008		
208.4	3.352	3.35	0.002	0.92	0.92	0	0.002	3.266	3.268	-0.002	0.17	0.17	-0.004	0.005		
206.5	3.384	3.385	0	0.91	0.91	0	0	3.239	3.239	0	0.19	0.19	0.001	0.001		
204.5	3.418	3.418	0	0.9	0.9	0	0	3.21	3.21	0	0.22	0.22	0	0		
202.7	3.449	3.451	-0.002	0.89	0.89	0	0.002	3.186	3.184	0.002	0.25	0.24	0.006	0.006		
200.8	3.481	3.483	-0.002	0.88	0.88	0	0.002	3.159	3.158	0.002	0.27	0.27	0.004	0.005		
199	3.512	3.513	-0.002	0.88	0.88	0	0.002	3.135	3.133	0.002	0.3	0.29	0.005	0.005		
197.3	3.541	3.543	-0.003	0.87	0.87	0	0.003	3.112	3.109	0.003	0.33	0.32	0.008	0.009		
195.6	3.569	3.572	-0.003	0.86	0.86	0	0.003	3.09	3.087	0.003	0.36	0.35	0.009	0.009		
194	3.597	3.601	-0.004	0.85	0.85	0	0.004	3.069	3.065	0.004	0.4	0.39	0.012	0.012		
192.4	3.624	3.628	-0.004	0.84	0.84	0	0.004	3.048	3.044	0.004	0.43	0.42	0.012	0.013		
190.9	3.649	3.654	-0.005	0.83	0.83	0	0.005	3.03	3.025	0.005	0.47	0.45	0.016	0.017		
189.3	3.677	3.68	-0.004	0.82	0.82	0	0.004	3.009	3.006	0.004	0.5	0.49	0.012	0.012		
187.9	3.7	3.705	-0.005	0.81	0.81	0	0.005	2.993	2.988	0.005	0.54	0.52	0.017	0.018		
186.4	3.726	3.73	-0.004	0.8	0.8	0	0.004	2.974	2.97	0.004	0.57	0.56	0.014	0.015		
185	3.75	3.754	-0.004	0.79	0.79	0	0.004	2.958	2.953	0.004	0.61	0.59	0.015	0.015		
183.7	3.772	3.777	-0.005	0.78	0.78	0	0.005	2.943	2.937	0.006	0.65	0.63	0.02	0.021		

182.3	3.796	3.8	-0.005	0.77	0.77	0	0.005	2.927	2.922	0.005	0.68	0.67	0.017	0.018
180.9	3.819	3.823	-0.003	0.76	0.76	0	0.003	2.91	2.907	0.003	0.72	0.7	0.013	0.013
179.6	3.842	3.845	-0.003	0.75	0.75	0	0.003	2.896	2.893	0.003	0.75	0.74	0.013	0.013
178.4	3.862	3.866	-0.004	0.74	0.74	0	0.004	2.883	2.879	0.004	0.8	0.78	0.018	0.019
177	3.886	3.888	-0.002	0.73	0.73	0	0.002	2.867	2.866	0.002	0.82	0.82	0.008	0.008
175.8	3.906	3.909	-0.002	0.72	0.72	0	0.002	2.855	2.853	0.002	0.87	0.85	0.01	0.011
174.5	3.928	3.929	-0.001	0.71	0.71	0	0.001	2.841	2.84	0.001	0.9	0.89	0.004	0.004
173.3	3.949	3.95	-0.001	0.7	0.7	0	0.001	2.829	2.828	0.001	0.94	0.93	0.004	0.004
172.1	3.969	3.97	-0.001	0.69	0.69	0	0.001	2.817	2.816	0.001	0.97	0.97	0.003	0.003
170.9	3.99	3.99	0	0.68	0.68	0	0	2.805	2.805	0	1.01	1.01	0	0
169.7	4.01	4.009	0.001	0.67	0.67	0	0.001	2.793	2.794	-0.001	1.04	1.05	-0.003	0.003
168.5	4.03	4.029	0.002	0.66	0.66	0	0.002	2.781	2.783	-0.002	1.08	1.09	-0.008	0.009
167.4	4.049	4.048	0.001	0.65	0.65	0	0.001	2.771	2.772	-0.001	1.12	1.13	-0.006	0.006
166.2	4.069	4.067	0.002	0.63	0.63	0	0.002	2.76	2.762	-0.002	1.15	1.16	-0.013	0.013
165	4.09	4.086	0.004	0.62	0.62	0	0.004	2.749	2.752	-0.004	1.18	1.2	-0.021	0.022
163.9	4.109	4.105	0.004	0.61	0.61	0	0.004	2.739	2.743	-0.004	1.22	1.24	-0.021	0.021
162.8	4.127	4.124	0.004	0.6	0.6	0	0.004	2.73	2.734	-0.004	1.26	1.28	-0.022	0.022
161.7	4.146	4.142	0.004	0.59	0.59	0	0.004	2.721	2.724	-0.004	1.3	1.32	-0.023	0.023
160.6	4.165	4.161	0.004	0.58	0.58	0	0.004	2.711	2.716	-0.004	1.34	1.36	-0.025	0.025
159.6	4.182	4.179	0.003	0.57	0.57	0	0.003	2.704	2.707	-0.003	1.38	1.4	-0.017	0.017
158.5	4.2	4.197	0.003	0.56	0.56	0	0.003	2.696	2.699	-0.003	1.42	1.44	-0.02	0.02
157.4	4.219	4.215	0.004	0.55	0.55	0	0.004	2.687	2.691	-0.004	1.46	1.48	-0.024	0.024
156.3	4.238	4.234	0.004	0.54	0.54	0	0.004	2.679	2.683	-0.004	1.49	1.52	-0.028	0.028
155.3	4.255	4.252	0.003	0.53	0.53	0	0.003	2.672	2.675	-0.003	1.54	1.56	-0.021	0.021
154.2	4.274	4.27	0.004	0.52	0.52	0	0.004	2.664	2.668	-0.004	1.58	1.6	-0.026	0.026
153.1	4.292	4.288	0.005	0.51	0.51	0	0.005	2.656	2.661	-0.005	1.61	1.65	-0.031	0.032
152.1	4.309	4.306	0.004	0.49	0.49	0	0.004	2.65	2.654	-0.004	1.66	1.69	-0.025	0.025
151.1	4.326	4.324	0.003	0.48	0.48	0	0.003	2.645	2.647	-0.003	1.71	1.73	-0.019	0.019
150	4.345	4.342	0.003	0.47	0.47	0	0.003	2.637	2.641	-0.003	1.75	1.78	-0.025	0.025
148.9	4.364	4.36	0.004	0.46	0.46	0	0.004	2.631	2.635	-0.004	1.79	1.82	-0.031	0.031
147.9	4.381	4.378	0.003	0.45	0.45	0	0.003	2.626	2.629	-0.003	1.84	1.87	-0.024	0.024
146.9	4.398	4.395	0.002	0.44	0.44	0	0.002	2.621	2.623	-0.002	1.89	1.91	-0.017	0.017
145.8	4.416	4.413	0.003	0.43	0.43	0	0.003	2.615	2.618	-0.003	1.94	1.96	-0.023	0.023
144.8	4.433	4.431	0.002	0.42	0.42	0	0.002	2.61	2.612	-0.002	1.99	2.01	-0.015	0.015
143.7	4.452	4.45	0.003	0.41	0.41	0	0.003	2.605	2.607	-0.003	2.04	2.06	-0.021	0.021
142.7	4.469	4.468	0.001	0.4	0.4	0	0.001	2.601	2.603	-0.002	2.1	2.11	-0.012	0.012
141.6	4.488	4.486	0.002	0.38	0.38	0	0.002	2.596	2.598	-0.002	2.15	2.16	-0.017	0.017
140.6	4.505	4.504	0.001	0.37	0.37	0	0.001	2.593	2.594	-0.001	2.21	2.22	-0.007	0.007
139.5	4.524	4.522	0.001	0.36	0.36	0	0.001	2.589	2.591	-0.001	2.26	2.27	-0.01	0.011
138.5	4.541	4.541	0	0.35	0.35	0	0	2.587	2.587	0	2.34	2.33	0.001	0.001
137.4	4.559	4.559	0	0.34	0.34	0	0	2.584	2.584	0	2.39	2.4	-0.001	0.001
136.3	4.578	4.578	0	0.33	0.33	0	0	2.581	2.581	0	2.46	2.46	-0.002	0.002
135.2	4.597	4.596	0	0.32	0.32	0	0	2.578	2.579	0	2.52	2.53	-0.002	0.002
134.1	4.615	4.615	0	0.31	0.31	0	0	2.577	2.577	0	2.6	2.6	-0.001	0.001
133	4.634	4.634	0	0.3	0.3	0	0	2.575	2.575	0	2.67	2.67	0.002	0.002
131.9	4.653	4.653	-0.001	0.29	0.29	0	0.001	2.574	2.574	0.001	2.75	2.75	0.006	0.006
130.8	4.672	4.673	-0.001	0.27	0.27	0	0.001	2.574	2.573	0.001	2.84	2.83	0.011	0.011
129.7	4.69	4.692	-0.002	0.26	0.26	0	0.002	2.575	2.573	0.002	2.93	2.91	0.018	0.018
128.5	4.711	4.712	-0.001	0.25	0.25	0	0.001	2.574	2.573	0.001	3.02	3.01	0.012	0.012
127.3	4.731	4.732	-0.001	0.24	0.24	0	0.001	2.575	2.574	0.001	3.11	3.1	0.007	0.007
126.1	4.751	4.752	-0.001	0.23	0.23	0	0.001	2.576	2.576	0.001	3.21	3.2	0.005	0.005
125	4.77	4.772	-0.002	0.22	0.22	0	0.002	2.58	2.578	0.002	3.33	3.31	0.02	0.02
123.7	4.792	4.793	-0.001	0.21	0.21	0	0.001	2.582	2.581	0.001	3.44	3.43	0.007	0.007
122.5	4.813	4.814	-0.001	0.2	0.2	0	0.001	2.587	2.585	0.001	3.57	3.56	0.012	0.012
121.3	4.833	4.835	-0.002	0.19	0.19	0	0.002	2.593	2.591	0.002	3.71	3.69	0.019	0.019
120	4.855	4.857	-0.002	0.18	0.18	0	0.002	2.599	2.597	0.002	3.85	3.83	0.015	0.015

118.7	4.877	4.879	-0.002	0.16	0.16	0	0.002	2.606	2.605	0.002	4	3.99	0.013	0.013
117.3	4.901	4.901	0	0.15	0.15	0	0	2.614	2.614	0	4.16	4.15	0.001	0.001
116.1	4.922	4.924	-0.002	0.14	0.14	0	0.002	2.628	2.625	0.003	4.36	4.34	0.021	0.021
114.7	4.945	4.947	-0.002	0.13	0.13	0	0.002	2.64	2.639	0.002	4.55	4.53	0.015	0.015
113.3	4.969	4.971	-0.002	0.12	0.12	0	0.002	2.656	2.654	0.002	4.76	4.75	0.014	0.014
111.8	4.995	4.995	-0.001	0.11	0.11	0	0.001	2.674	2.674	0.001	4.99	4.98	0.004	0.004
110.4	5.018	5.02	-0.002	0.1	0.1	0	0.002	2.698	2.697	0.002	5.25	5.24	0.011	0.011
108.9	5.044	5.045	-0.001	0.09	0.09	0	0.001	2.726	2.725	0.001	5.53	5.52	0.01	0.01
107.4	5.069	5.071	-0.002	0.08	0.08	0	0.002	2.761	2.759	0.002	5.84	5.83	0.013	0.013
105.9	5.095	5.098	-0.003	0.06	0.06	0	0.003	2.805	2.802	0.003	6.19	6.17	0.019	0.019
104.2	5.124	5.126	-0.002	0.05	0.05	0	0.002	2.859	2.857	0.002	6.57	6.56	0.01	0.01
102.6	5.151	5.154	-0.003	0.04	0.04	0	0.003	2.934	2.93	0.003	6.99	6.98	0.013	0.013
100.8	5.182	5.183	-0.002	0.03	0.03	0	0.002	3.035	3.033	0.002	7.46	7.46	0.006	0.006
99.1	5.211	5.214	-0.003	0.02	0.02	0	0.003	3.194	3.191	0.003	8	7.99	0.007	0.008
97.3	5.241	5.245	-0.004	0.01	0.01	0	0.004	3.501	3.497	0.004	8.6	8.6	0.005	0.006
95.3	5.275	5.277	-0.002	0	0	0	0.002	0	0	0	0	0	0	0
93.4	5.308	5.311	-0.003	-0.01	-0.01	0	0.003	0	0	0	0	0	0	0
91.3	5.343	5.346	-0.002	-0.02	-0.02	0	0.002	0	0	0	0	0	0	0
89.1	5.381	5.382	-0.001	-0.03	-0.03	0	0.001	0	0	0	0	0	0	0
86.8	5.42	5.42	0	-0.05	-0.05	0	0	0	0	0	0	0	0	0
84.5	5.459	5.46	-0.001	-0.06	-0.06	0	0.001	0	0	0	0	0	0	0
81.9	5.503	5.501	0.002	-0.07	-0.07	0	0.002	0	0	0	0	0	0	0
79.2	5.549	5.545	0.004	-0.08	-0.08	0	0.004	0	0	0	0	0	0	0
76.4	5.597	5.591	0.006	-0.09	-0.09	0	0.006	0	0	0	0	0	0	0
73.4	5.648	5.639	0.008	-0.1	-0.1	0	0.008	0	0	0	0	0	0	0
70.4	5.699	5.691	0.008	-0.11	-0.11	0	0.008	0	0	0	0	0	0	0
67.3	5.751	5.745	0.006	-0.12	-0.12	0	0.006	0	0	0	0	0	0	0
65.3	5.785	5.803	-0.017	-0.13	-0.13	0	0.017	0	0	0	0	0	0	0

AVERAGE SUM SQUARES

OF RESIDUALS 1 2.9E-06 1 7.8E-06 1.3E-05 1 3.0E-07 2 1.8E-05 2.3E-04

NUMBER OF TITRATIONS = 1

TOTAL NUMBER OF POINTS = 116