Potentiometric and Electrochemical studies for the interaction of Zinc (II), Lead (II), Cadmium (II) with HEPES and HEPPSO as Zwitterionic Buffer Ligands at Different Temperature

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ABSTRACT

The complexation of the divalent transition metal ions Zn (II), Pb (II) or Cd (II) with two important biologically zwitterionic buffers (N-[2-hydroxyethyl] piperazine-N'-[2-ethanesulfonic acid]) (HEPES) and (N-[2-hydroxyethyl] piperazine-N'-[2-hydroxy-propanesulfonic acid]) (HEPPSO) in an aqueous medium, were studied using potentiometric pH titration in 1:1 ratio at four different temperatures 288 K, 298 K, 308 K and 318 K at ionic strength 0.1 $molL^{-1}$ KNO_3. The formation constants and thermodynamic parameters of different protonated, normal, monohydroxy and dihydroxy complexes for the binary systems M(II) + HEPES and M(II) + HEPPSO have been evaluated. The electrochemical behavior of the free Pb(II) and its binary complexes with HEPES and HEPPSO was studied by cyclic voltammetry on glassy carbon electrode. Upon temperature elevation the rate of the reduction process of the Pb^{2+}-HEPPSO is higher than that of Pb^{2+}-HEPES. The diffusion coefficient, the activation energies and the standard rate constant (Ks) for the diffusion process of Pb(II) complexes were calculated.

1. Introduction

The temperature changes have a great effect on the dissociation constant of zwitterionic buffers; especially the measurements of the pH of a physiological buffer are an integral part of clinical diagnosis[1-9].

Studies involving metal ions in solution, which require pH control, are inevitably subject to the possibility of buffer interferences as a result of complexation. Many conflicting data could be happened for example, when studding system contains metal + cation protein systems at the same time, conflicting data can be produced might be due to include the presence of metal–buffer complexes. Metal complexes with Zwittherionic buffers may be formed through hydroxyl groups in addition to a primary nitrogen donor atom [10].

For the standardization of pH and control of acidity in the physiological region of pH 7 to 9, Good et al.[1] and Ferguson et al. [2] have listed hydrogen buffers which are N-substituted amino acids compatible with common biological media.

Two of the potentially useful zwitterionic buffers for use in biochemistry are N-2- hydroxy ethyl piperazine –N-ethansulfonic acid (HEPES) and N-2- hydroxy ethyl piperazine –N'-2-hydroxypropane sulfonic acid (HEPPSO).

Zwitterionic buffers can be used in biological, biochemical and environment studies [11]. HEPES is widely used in cell culture when compared to bicarbonate buffers, while HEPPSO is an efficient separator in protein resolution [12].

Azab et al. [13-22] have studied the interaction of different types of zwitterionic buffers and many biologically important molecules.

The aim of this work is to study the complexing properties of zwitter ionic buffers HEPES and HEPPSO in presence of metal ions Zn (II), Pb (II), Cd (II) at different temperatures via potentiometric methods to compare the stabilities of the formed complexes at various temperatures. Also the electrochemical behavior of the examined complexes using cyclic voltammetric measurements has been studied.

The structures of the studied zwitterionic buffers in this work are shown in Chart 1.

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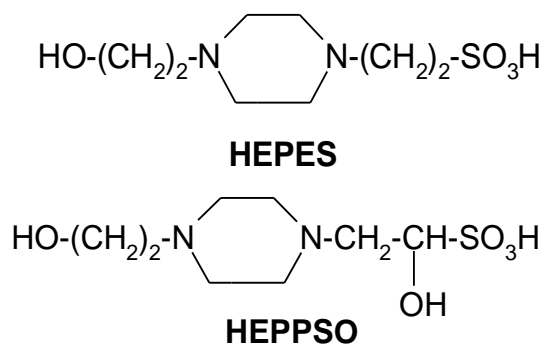E-mail addresses: rasha.abdalla@suezuniv.edu.eg (Rasha M. Kamel)

HO-(CH$_2$)$_2$-N〔   〕N-(CH$_2$)$_2$-SO$_3$H

HEPES

HO-(CH$_2$)$_2$-N〔   〕N-CH$_2$-CH-SO$_3$H
                                    |
                                   OH

HEPPSO

Chart 1: The structures of the studied zwitterionic buffers

2. Materials and methods

2.1 Materials and Solutions

HEPES and HEPPSO were purchased from Sigma Chemical Co. and were used without purification. Zn(NO$_3$)$_2$6H$_2$O, Pb(NO$_3$)$_2$ and Cd(NO$_3$)$_2$3H$_2$O was from the Sigma chemical Co. Stock solutions (0.01 molL^{-1}) of metal salts were prepared by dissolving precisely weighed amount of the salt in bidistilled water. The concentrations of the metal ion stock solutions were determined complexometrically by ethylenediamine tetracetic acid dissodium salt (EDTA) using suitable indicators [23]. The ionic strength of the studied solutions was adjusted to 0.1 molL^{-1} using a stock solution of KNO$_3$. KNO$_3$ was from Merck AG.

The solution titrated can be presented according to the following scheme: (a) 4x10^{-3} molL^{-1} HNO$_3$ + 1x10^{-3} molL^{-1} HEPES; (b) 4x10^{-3} molL^{-1} HNO$_3$ + 1x10^{-3} molL^{-1} HEPES + 1x10^{-3} molL^{-1} M (II); (c) 4x10^{-3} molL^{-1} HNO$_3$ + 1x10^{-3} molL^{-1} HEPPSO; (d) 4x10^{-3} molL^{-1} HNO$_3$ + 1x10^{-3} molL^{-1} HEPPSO + 1x10^{-3} molL^{-1} M (II).

Where M (II) = Zn (II), Pb (II) and Cd (II). At least four titration were performed for each system at different temperatures (288 K, 298 K, 308 K and 318 K).

In electrochemical measurements, a sample volume of 25 ml containing: (a) 1x10^{-3} molL^{-1} Pb (II); (b) 1x10^{-3} molL^{-1} Pb (II) + 1x10^{-3} molL^{-1} HEPES; (c) 1x10^{-3} molL^{-1} Pb (II) + 1x10^{-3} molL^{-1} HEPPSO. The ionic strength of the studied solutions was adjusted at 0.1 molL^{-1} using KNO$_3$ solution.

In Cyclic voltammetric measurements the solution was purged with nitrogen for 120 s and then the potential was scanned at scan rate 100 mV s^{-1} from (-0.3 to -0.9 V). The solutions of the complexes were thermostated at the required temperature, for measurements of the temperature effect.

2.2 Apparatus

Potentiometric pH measurements were performed on the solutions in a double-walled glass vessel at 288 K, 298 K, 308 K and 318 K with a commercial Fisher combined electrodes, and a magnetic stirrer was used.

A Fisher Accumet pH/ion meter model 325 MP was used. The temperature was controlled using a thermostat.

Cyclic voltammetry (CV) is collected using EG and G Princeton applied research, potentiostat/galvanostat model 263 with a single compartment voltammetric cell equipped with a glassy carbon (GC) working electrode (area = 0.1963 cm^2) embedded in a resin, a Pt-wire counter electrode, and Ag\AgCl electrode as reference electrode.

pKa values of the investigated ligands were determined in water from the overall protonation constants ☐$_1$ and ☐$_2$ calculated by the linearization method of Irving and Rossotti [24].

3. Result and Discussion

The Chemical and biological activity of zwitterionic buffers would be expected to vary with the degree of ionization. These molecules may exist in a great number of distinct ionization states according to the pH of the solution. Temperature variation has an important role in determining the dissociation of such molecules in aqueous medium.

The second stage dissociation constants of the protonated amine group (-N$^+$H) pKa$_2$ were estimated at four different temperatures (288 K, 298 K, 308 K and 318 K) for the studied two ligands HEPES and HEPPSO. In fact the two zwitterionic buffers have two dissociation constants (pKa$_1$, PKa$_2$). The acidic pKa$_1$ is due to the dissociation of sulfonic acid group which take place in acidic medium (pH 2.0 – 3.0). We have investigate only pKa$_2$ value which occur in the physiological pH range and determine the binding ability and the useful pH range of the two biologically important buffer ligands HEPES and HEPPSO [25].

The thermodynamic parameters associated with temperature variation were analyzed by applying the Van't Hoff equation:

$$lnK = -\Delta H/RT + \Delta S/R \qquad (1)$$
$$\Delta G = -RT\, lnK \qquad (2)$$

Where K is the dissociation constants or formation constant of complexes at corresponding temperature and R is the gas constant, in which ΔH and ΔS of reaction could be determined from the linear relationship between lnK and the reciprocal absolute temperature. The free energy (ΔG) could be calculated by Eq. (2).

Table 1 depicts the obtained values for the ionization process and the calculated thermodynamic parameters associated with the dissociation of HEPES and HEPPSO. Generally the second stage dissociation constants of the two ligands decrease with temperature elevation. This makes HEPES and HEPPSO more effective buffering agent for maintaining enzyme structure and function at low temperatures, where the dissociation process is exothermic for HEPES ligand, the amount of heat liberated is more than HEPPSO by about 4600 KJmol^{-1}, which may be attributed to the presence of –OH group in HEPPSO. The entropy change slightly positive, but it is slightly more positive for HEPPSO than HEPES which may be attributed to release of less water molecules upon dissociation of the ligand, and destroying of the salvation shell.
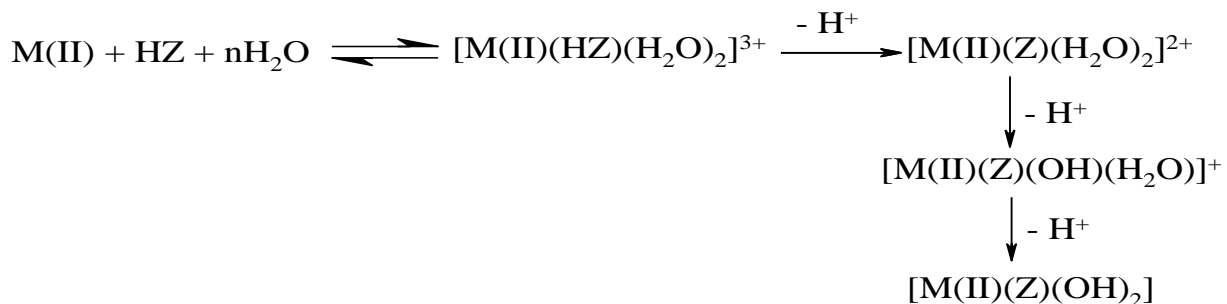
$$M(II) + HZ + nH_2O \rightleftharpoons [M(II)(HZ)(H_2O)_2]^{3+} \xrightarrow{-H^+} [M(II)(Z)(H_2O)_2]^{2+}$$

$$\downarrow -H^+$$

$$[M(II)(Z)(OH)(H_2O)]^+$$

$$\downarrow -H^+$$

$$[M(II)(Z)(OH)_2]$$

Chart 2: The predicted interaction of M (II) with HEPES and HEPPSO (HZ)

Table 1: Apparent second stage dissociation constant (pKa_2) for HEPES and HEPPSO zwitterionic buffers at different temperatures and the accompanied thermodynamic parameters (ΔG, ΔH and ΔS), at I = 0.1 $molL^{-1}$ KNO_3.

Z	Temp.	pKa_2	ΔH $(KJmol^{-1})$	ΔS $(J/mol.k)$	ΔG $(KJmol^{-1})$
HEPES	288 K	7.72±0.02			42.57
	298 K	7.60±0.02	-1.86×10^4	83.09	43.36
	303 K	7.52±0.02			43.62
	318 K	7.40±0.02			45.06
HEPPSO	288 K	7.94±0.03			43.78
	298 K	7.85±0.03	-1.40×10^4	103.20	44.79
	303 K	7.78±0.03			45.13
	318 K	7.70±0.03			46.88

± refers to three times standard deviation (3s)
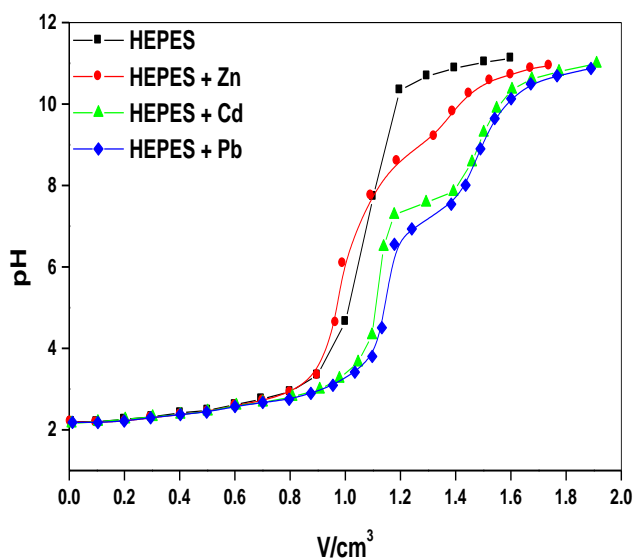
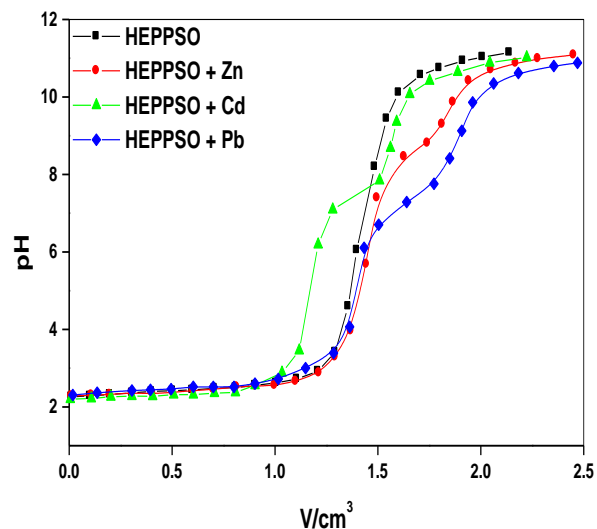**Fig. 1:** Potentiometric pH-Titration Curves for M(II)+ HEPES System, I = 0.1 $molL^{-1}$ and at 25 ± 0.1 ^oC

Fig. 2: Potentiometric pH-Titration Curves for M(II)+ HEPPSO System, I = 0.1 $molL^{-1}$ and at 25 ± 0.1 ^oC

From the potentiometric titration curves for Zn^{2+}, Cd^{2+} and Pb^{2+} with HEPES and HEPPSO (Fig. 1,2), the formation constants for the different complex species formed by Zn^{2+}, Cd^{2+} and Pb^{2+} ions with the zwitterionic buffer HEPES and HEPPSO are calculated (Table 2,3) according to Chart 2.

During the HYPERQUAD refinement all the possible hydrolysis reactions of Pb (II) ions have been taken into consideration. All the calculations were carried out in the pH ranges where no Pb (II) hydroxide precipitation occurs. We got a good standard deviation values for the considered model of interaction of Pb (II) with HEPES or HEPPSO.

Table 2: Formation constants for the normal, protonated and hydroxo binary M(II) + HEPES complexes at different temperatures and I = 0.1 $molL^{-1}$ KNO_3.

Metal Ion	Temp.	$logK\dfrac{M}{[M(HZ)]^+}$	$logK\dfrac{[M(HZ)]^+}{[M(Z)]}$	$logK\dfrac{[M(Z)]}{[M(Z)(OH)]^-}$	$logK\dfrac{[M(Z)(OH)]^-}{[M(Z)(OH)_2]^{2-}}$
Zn	288 K	7.07±0.02	3.42±0.01	3.47±0.02	7.35±0.03
	298 K	6.73±0.02	3.36±0.01	3.23±0.02	7.05±0.03
	303 K	6.43±0.02	3.34±0.01	3.03±0.02	6.85±0.03
	318 K	6.01±0.02	3.26±0.01	2.76±0.02	6.60±0.03
Cd	288 K	4.88±0.02	3.29±0.01	3.22±0.02	5.60±0.03
	298 K	4.65±0.02	3.15±0.01	3.29±0.02	5.73±0.03
	303 K	4.50±0.02	3.00±0.01	3.39±0.02	5.90±0.03
	318 K	4.29±0.02	2.87±0.01	3.57±0.02	6.10±0.03
Pd	288 K	6.22±0.02	3.60±0.01	3.67±0.02	7.95±0.03
	298 K	6.10±0.02	3.40±0.01	3.65±0.02	7.88±0.03
	303 K	6.00±0.02	3.31±0.01	3.64±0.02	7.70±0.03
	318 K	5.91±0.02	2.99±0.01	3.61±0.02	7.58±0.03

± refers to three times standard deviation (3s)

Table 3: Formation constants for the normal, protonated and hydroxo binary M(II) + HEPPSO complexes at different temperatures and I = 0.1 $molL^{-1}$ KNO_3.

Metal Ion	Temp.	$logK\dfrac{M}{[M(HZ)]^+}$	$logK\dfrac{[M(HZ)]^+}{[M(Z)]}$	$logK\dfrac{[M(Z)]}{[M(Z)(OH)]^-}$	$logK\dfrac{[M(Z)(OH)]^-}{[M(Z)(OH)_2]^{2-}}$
Zn	288 K	5.67±0.02	3.40±0.01	3.03±0.02	6.05±0.03
	298 K	5.85±0.02	3.43±0.01	3.32±0.02	6.36±0.03
	303 K	6.00±0.02	3.50±0.01	3.68±0.02	6.70±0.03
	318 K	6.12±0.02	3.62±0.01	4.02±0.02	7.01±0.03
Cd	288 K	4.25±0.02	3.30±0.01	2.83±0.02	6.10±0.03
	298 K	4.53±0.02	3.31±0.01	3.25±0.02	6.71±0.03
	303 K	4.92±0.02	3.33±0.01	3.77±0.02	7.15±0.03
	318 K	5.11±0.02	3.34±0.01	4.25±0.02	7.70±0.03
Pd	288 K	8.63±0.02	5.20±0.01	4.47±0.02	7.60±0.03
	298 K	8.00±0.02	4.55±0.01	3.92±0.02	7.14±0.03
	303 K	7.65±0.02	4.00±0.01	3.37±0.02	6.70±0.03
	318 K	6.98±0.02	3.35±0.01	3.06±0.02	6.25±0.03

Inspection of the data reveals that generally the trend of stability increase in the order $Zn^{2+} > Pb^{2+} > Cd^{2+}$ for HEPES buffer ligand. While for HEPPSO ligand the order is $Pb^{2+} > Zn^{2+} > Cd^{2+}$ [26].

The basicity effect as well as the participation of hydroxo group of HEPPSO in the coordination with metal ions play an important role at elevated temperatures which reflect itself in observing the higher formation constants of metal ion HEPPSO binary protonated complexes than that of metal ion – HEPES especially in the case of Pb(II).

The Zn-HEPPSO and Cd-HEPPSO monohydroxy and dihydroxy species become more stable at high temperature than the corresponding complexes with HEPES. On the other hand, the Pb-HEPPSO mono and dihydroxy species favor low temperatures to become more stable than Pb-HEPES complex hydroxyl species.

Generally the interaction of Zn^{2+} with HEPES is of exothermic nature, while for HEPPSO the interaction is of endothermic type as indicated in Table 4.

In Table 5 one can observe the reaction of Pb^{2+} with HEPPSO is more exothermic than that with HEPES, while the binary complexes of Pb-HEPPSO are more ordered than Pb-HEPES.

For the protonated and normal complexes of Cd-HEPES the process is exothermic, while for mono and dihydroxy species the process becomes endothermic. The complexes of Cd-HEPES become more ordered than Cd-HEPPSO as shown in Table 6.

The formation of the Zn-HEPES different complex species is exothermic where the amount of released heat during complexation follow the order: Zn^{2+}-H(HEPES) > Zn^{2+}-H(HEPES)(OH)$_2$ > Zn^{2+}-(HEPES)(OH) > Zn^{2+}-(HEPES), while upon interaction of Zn^{2+} with HEPPSO the reactions become endothermic where the order according to the absorbed amount of heat is: Zn^{2+}-(HEPPSO)(OH)$_2$ > Zn^{2+}- (HEPPSO)(OH) > Zn^{2+}-H(HEPPSO) > Zn^{2+}-(HEPPSO).

Table 4: Thermodynamic parameters associated with the complex formation of Zn(II) + HEPES and Zn(II) + HEPPSO at I = 0.1 molL^{-1} KNO$_3$.

Nature of Complex	Temp.	Zn(II) + HEPES			Zn(II) + HEPPSO		
		ΔH (KJmol^{-1})	ΔS (J/mol.k)	ΔG (KJmol^{-1})	ΔH (KJmol^{-1})	ΔS (J/mol.k)	ΔG (KJmol^{-1})
[Zn(HZ)]$^+$	288 K			38.98			31.26
	298 K	-6.22×10^4	-81.0	38.40	2.63×10^4	200.28	33.37
	303 K			37.30			34.80
	318 K			36.01			36.67
[Zn(Z)]	288 K			18.85			18.74
	298 K	-9.17×10^3	33.62	19.17	1.33×10^4	110.86	19.57
	303 K			19.37			20.30
	318 K			19.53			21.69
[Zn(Z)(OH)]$^-$	288 K			19.13			16.70
	298 K	-4.16×10^4	-78.12	18.42	5.88×10^4	262.51	18.94
	303 K			17.57			21.34
	318 K			16.54			24.09
[Zn(Z)(OH)$_2$]$^{2-}$	288 K			40.53			33.36
	298 K			40.22			36.28
	303 K	-4.35×10^4	-10.92	39.74	5.68×10^4	313.25	38.87
	318 K			39.55			42.01

Table 5: Thermodynamic parameters associated with the complex formation of Pb(II) + HEPES and Pb(II) + HEPPSO at I = 0.1 molL^{-1} KNO$_3$.

Nature of Complex	Temp.	Pb(II) + HEPES			Pb(II) + HEPPSO		
		ΔH (KJmol^{-1})	ΔS (J/mol.k)	ΔG (KJmol^{-1})	ΔH (KJmol^{-1})	ΔS (J/mol.k)	ΔG (KJmol^{-1})
[Pb(HZ)]$^{+}$	288 K			44.22			47.58
	298 K	-1.81x10^4	55.91	45.07	-9.54x10^4	-166.77	45.64
	303 K			45.25			44.38
	318 K			46.20			41.83
[Pb(Z)]	288 K			19.85			28.67
	298 K	-3.53x10^4	-53.42	19.39	-1.08x10^5	-277.44	25.69
	303 K			19.20			23.20
	318 K			17.91			20.07
[Pb(Z)(OH)]$^{-}$	288 K			20.23			24.64
	298 K	-3.48x10^3	58.21	20.82	-8.29x10^4	-203.92	22.36
	303 K			21.11			19.55
	318 K			21.63			18.33
[Pb(Z)(OH)$_2$]$^{2-}$	288 K			43.83			41.90
	298 K	-2.26x10^4	74.10	44.96	-7.94x10^4	-130.77	40.73
	303 K			44.67			38.87
	318 K			45.42			37.45

Generally the complexes of Zn-HEPES are more ordered than that of the corresponding Zn-HEPPSO.

Inspection of the electrochemical data obtained from Figure 3 and collected in Table 7 indicates that the reduction potentials of the two complexes are shifted to more negative with respect to the free lead metal ion. The reduction potential of the free metal ion is shifted by 118.50 mV compared to Pb-HEPES complex while the shift is 134.28 mV also to more negative for the binary complex of Pb-HEPPSO. This is in agreement with the potentiometric measurements which confirmed the greater stability of Pb-HEPPSO compared to Pb-HEPES.

This behavior can be attributed to the possible participation of the OH-group of HEPPSO during the complexation reaction with Pb^{2+} ions. The shape of the cyclic voltammograms for both free and complexes Pb(II) ions indicates quasireversible electrochemical behavior at the glassy carbon electrode at this experimental condition.

The reduction current decreases upon complexation which may be attributed to the low adsorption probability of the formed complex species, where the Pb-HEPES is more adsorbed than Pb-HEPPSO complex.
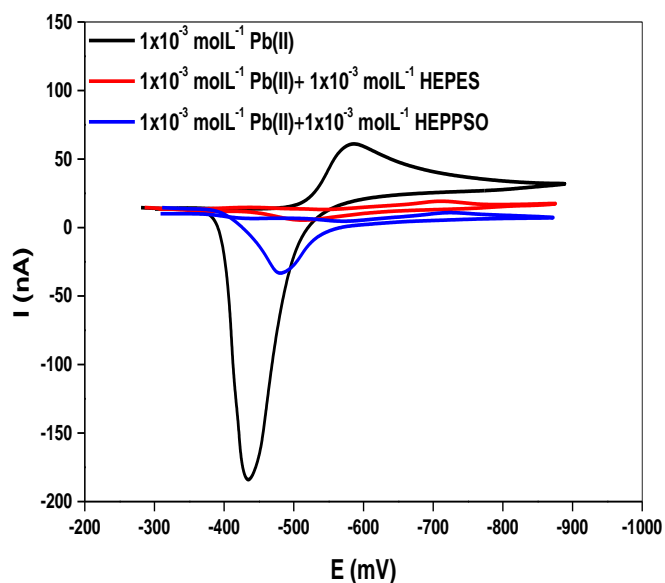

Fig. 3: Cyclic Voltammograms for Pb(II) with HEPES and HEPPSO, I = 0.1 molL^{-1} KNO$_3$, Scan Rate = 100 mVs^{-1}, pH = 6 and at 25 ± 0.1 $^{\circ}$C.

Table 6: Thermodynamic parameters associated with the complex formation of Cd(II) + HEPES and Cd(II) + HEPPSO at I = 0.1 molL^{-1} KNO$_3$.

Nature of Complex	Temp.	Cd(II) + HEPES			Cd(II) + HEPPSO		
		ΔH (KJmol^{-1})	ΔS (J/mol.k)	ΔG (KJmol^{-1})	ΔH (KJmol^{-1})	ΔS (J/mol.k)	ΔG (KJmol^{-1})
[Cd(HZ)]$^+$	288 K			26.91			23.43
	298 K	-3.42x10^4	-25.66	26.35	5.13x10^4	260.4	25.84
	303 K			26.10			28.54
	318 K			25.71			30.62
[Cd(Z)]	288 K			18.14			18.19
	298 K	-2.48x10^4	-23.36	17.97	2.42x10^3	71.61	18.88
	303 K			17.40			19.31
	318 K			17.20			20.01
[Cd(Z)(OH)]$^-$	288 K			17.75			15.60
	298 K	2.09x10^4	133.83	18.77	8.44x10^4	347.52	18.54
	303 K			19.66			21.87
	318 K			21.39			25.47
[Cd(Z)(OH)$_2$]$^{2-}$	288 K			30.08			33.36
	298 K	2.98x10^4	210.42	32.69	9.31x10^4	441.15	36.28
	303 K			34.22			41.48
	318 K			36.01			46.14

Table 7: Voltammetric characteristics of 1x10^{-3} molL^{-1} Pb(II), Pb(II)-HEPES and Pb(II)-HEPPSO at I = 0.1 molL^{-1} KNO$_3$ and at 25.0 ± 0.1 ^{o}C.

System	-Ep$_c$ (mV)	-ip$_c$ (nA)	-Ep$_a$ (mV)	-ip$_a$ (nA)
Pb(II)	-581.5±2.00	-44.80±2.00	-436.8±0.90	193.2±1.90
Pb(II)-HEPES	-640.0±2.00	-8.80±2.00	-484.2±1.00	16.0±2.00
Pb(II)-HEPPSO	-618.0±1.90	-14.30±1.90	-477.0±1.50	32.0±2.10

± Uncertainties refer to 3 times the standard deviation in measured potentials 3s.

Table 8: Voltammetric characteristics of Pb(II)-HEPES and Pb(II)-HEPPSO complexes at I = 0.1 molL^{-1} KNO$_3$ and at different temperatures.

System	Temp.	-Ep$_c$ (mV)	-ip$_c$ (nA)	-Ep$_a$ (mV)	-ip$_a$ (nA)
Pb(II)-HEPES	288 K	-657.86±2.50	7.48±2.00	-484.16±1.90	11.35±2.00
	298 K	-640.00±2.50	8.80±2.10	-484.16±1.00	16.00±1.90
	318 K	-605.26±1.80	10.98±1.90	-484.16±1.60	26.45±1.80
Pb(II)-HEPPSO	288 K	-642.10±2.00	14.19±1.90	-476.27±1.80	23.20±1.90
	298 K	-618.00±1.90	14.30±2.00	-477.00±1.50	32.00±2.00
	318 K	-573.58±1.80	14.56±2.00	-478.90±1.60	49.36±2.10

± Uncertainties refer to 3 times the standard deviation in measured potentials 3s.

The oxidation current is reduced greatly in the case of Pb-HEPES than Pb-HEPPSO which may be attributed to the low adsorptivity of the Pb-HEPES binary complex than Pb-HEPPSO on the surface of glass electrode.

The cyclic voltammograms for Pb-HEPES and Pd-HEPPSO binary complexes on the surface of glassy carbon electrode at different temperature is depicted in Figure 4, 5.

The voltammetric characteristics of Pb(II)-HEPES and Pb(II)-HEPPSO binary complexes at different temperatures (288, 298 and 318 K) are collected in Table 8.

The diffusion coefficients (D) for the Pb^{2+} complexes were determined using Randles-Shevichik equation [27].

$$I = 0.4463\ F^{3/2}\ R^{-1/2}\ T^{-1/2}\ n^{3/2}\ A\ C\ D^{1/2}\ v^{1/2} \qquad (3)$$

According to the reduction process

$$Pb^{2+} + 2e \rightarrow Pb$$
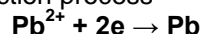
The activation energies for the diffusion (∆U) of Pb(II)-complexes (Table 8) are calculated from the equation.

$$-\Delta U/2.303\ R = \partial \log D\ /\ \partial\ (1/T) \qquad (4)$$

According to the assumption of Nicholson [28] dealing with the kinetic parameters of quasireversible process on the basis of cyclic voltammetry.

Inspecting the data obtained in Table 9, it is clearly observed that the diffusion coefficient of Pb-HEPPSO is higher than Pb-HEPES on the glassy electrode surface. The activation energy for diffusion of Pb-HEPPSO is greatly lower than that for Pb-HEPES i.e., the energy barrier for the reduction of this complex is lower than that for Pb-HEPPSO.
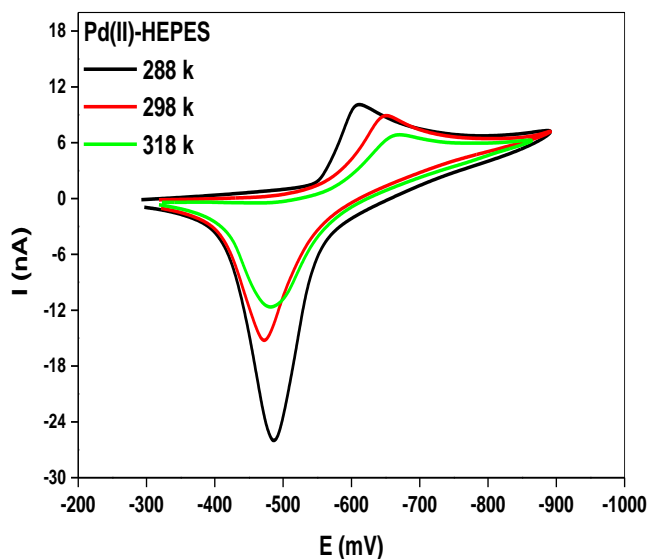

Fig. 4: Effect of Temperature on Cyclic Voltammograms for Pb(II)-HEPES, I = 0.1 molL^{-1} KNO$_3$ and Scan Rate = 100 mVs^{-1}
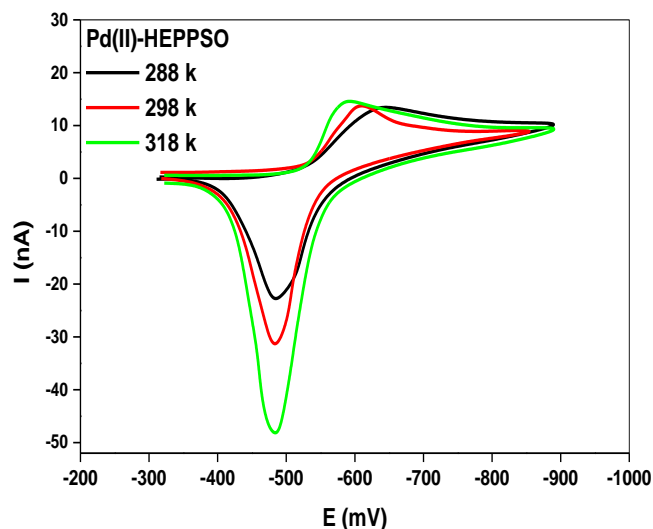

Fig. 5: Effect of Temperature on Cyclic Voltammograms for Pb(II)-HEPPSO, I = 0.1 molL^{-1} KNO$_3$ and Scan Rate = 100 mVs^{-1}

The standard rate constant of the electrode process is related to the function ψ as follows:

$$\psi = \frac{k_s \left(\dfrac{D_{ox}}{D_{red}}\right)^{\alpha/2}}{\pi^{1/2} D_{ox}^{1/2} \left(\dfrac{nF}{RT}\right)^{1/2} \nu^{1/2}} \qquad (5)$$

Where ψ is a function related to the difference between the peak potentials, K_s is the standard rate constant of the electrode process (s^{-1}) (Table 10) and α is the transfer coefficient. The value of K_s for the two complexes reveal that the electroreduction process for Pb-HEPPSO has a slower rate than Pb-HEPES, which indicate that the former one is a stronger bond complex than Pb-HEPES, since the smaller and stronger bond complexes require higher rearrangement energy and in consequence the electroreduction proceeds via slower rate [29].

4. Conclusion

The present work describes complexation of the divalent transition metal ions Zn^{2+}, Cd^{2+} and Pb^{2+} with zwitterionic buffers HEPES and HEPPSO in an aqueous medium. The formation constants and thermodynamic parameters of different protonated, normal, monohydroxy and dihydroxy complexes for the binary systems M(II) + HEPES and M(II) + HEPPSO have been evaluated. The electrochemical behavior of the free Pb(II), its binary complexes with HEPES and HEPPSO at different temperatures was studied by cyclic voltammetry on glassy carbon electrode.

References

[1] N.E. Good, G. D. Winget, T. N. Connolly, S. Izawa and R. M. M. Singh, Biochemistry 5 (1996) 467-477.

[2] W. J. Ferguson, K. I. Braunschwieger, W. R. Braunschwieger, J. R. Smith. J. J. McCormick, C. C. Wasman, N. P. Jarvis, D. H. Bell and N. E. Good, Anal. Biochemistry 104 (1980) 300-310.

[3] R. N. Roy, C. P. Moore, M. D. Bliss, S. Patel, A. Kilker, J. A. Carlsten, W. S. Good and L. N. Roy, J. Chem. Thermodynamics 29 (1997) 749-756.

[4] E. J. King, J. Am. Chem. Soc. 67 (1945) 2178-2182.

[5] R. N. Roy, J. J. Gibbons, C. W. Krueger, G. Jr. La Cross, J. Chem. Thermodynamics 9 (1977) 325-332.

[6] R. N. Roy, J. Bice, J. Greer, J. A. Carlsten, J. Smithson, W. S. Good, C. P. Moore, L. N. Roy and K. M. Kubler, J. Chem. Eng. Data 42 (1997) 41-44.

[7] R. N. Roy, R. A. Robinson and R. G. Bates, J. Am. Chem. Soc. 95 (1973) 8231-8235.

[8] R. N. Roy, C. P. Moore, J. A. Carlsten, W. S. Good, P. Harris, J. M. Rook, L. N. Roy and K. M. Huhler, Journal of solution chemistry 26 (1997) 1209-1216.

[9] R.N. Roy, L.N. Roy, S.R.LeNoue, J. Chem. Thermodynamics 38 (2005) 413-417.

[10] M. Tahaa, R. A. Saqr, A. T. Ahmed, J. Chem. Thermodynamics 39 (2007) 304-308.

[11] C.M. H. Ferreira, I. S. S, Pinto, E. V. Soaresbc and H. M. V. M. Soares RSC Adv. 5 (2015) 30989–31003

[12] S.C. Baicu and M.J. Taylor Cryobiology 45 (1) (2002) 33–48.

[13] Z. M. Anwar and H. A. Azab, J. Chem. Eng. Data 46 (2001) 34-40.

[14] Z. M. Anwar, H. A. Azab, J. Chem. Eng. Data 44 (1999) 1151-1157.

[15] H. A. Azab, F. S. Deghaidy, A. S. Orabi and N. Y. Farid, J. Chem. Eng. Data 45 (2000) 709.

[16] H. A. Azab, A. S. Orabi and E. T. Abdel-Salam, J. Chem. Eng. Data 46 (2001) 346-352.

[17] Z. M. Anwar, H. A. Azab, J. Chem. Eng. Data 46 (2001) 613-618.

[18] H. A. Azab and Z. M. Anwar, J. Chem. Eng. Data 57 (2012) 2890-2895.

[19] H. A. Azab, Z. M. Anwar, S. S. al-Deyab and R. M. Kamel, J. Chem. Eng. Data 56 (2011) 1960.

[20] H. A. Azab, Z. M. Anwar, S. S. al-Deyab, I. I. Abd El-Gawad and R. M. Kamel, J. Chem. Eng. Data 56 (2011) 2613.

[21] H. A. Azab, Z. M. Anwar and R. M. Kamel, Journal of Solution Chemistry 45(7) (2016) 1095.

[22] H. A. Azab, Z. M. Anwar and R. M. Kamel, Journal of Solution Chemistry 45(10) (2016) 1516.

[23] F. J. Welcher, "The Analytical Uses of Ethylene diaminetetraacetic acid" D.Von. Nostrand Co.,Inc., Princeton (1965).

[24] H. Irving, H. S. Rossotti, J. Chem. Soc. (1953) 3397-3405.

[25] M.V.M. Helena Soares, C.F.L. Paula Conde, Analytica Chimica Acta 421 (2000) 103–111.

[26] Z. M. Anwar, J. Chin. Chem. Soc. 52 (2005) 863-871

[27] Z. Galus, "fundamentals of electrochemical analysis", Ellis Horwood, London (1994).

[28] R. S. Nicholsom, Anal. Chem. 37 (1965) 1351-1355.

[29] F. A. Al-Saif, Int. J. Electrochem. Sci. 9 (2014) 398 – 417.