Construction and Charactrization of Chloropromazine hydrochloride Selective Electrode Based on Complex Chloropromazine hydrochloride – Sodium tetra phenyl borate on a PVC Matrix .

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Abstract

Chloropromazine hydrochloride selective electrodes were construct based on a complex chloropromazine hydrochloride-sodium tetra phenyl borate as an active material using the plasticizers: di-butyl phthalate(DBPH),O-Nitro phenyl octyl ether (o-NPOE) in a PVC matrix membrane. The properties of the electrodes were studied .A linear range of electrode based on DBPH found from 5×10^{-4}-10^{-2} M with a Nernstian slope of 54.1 mV/decade and correlation coefficient of 0.9996,the detection limit was 2×10^{-4}M, and the lifetime was around 72 days. The electrode based on o-NPOE as a plasticizer showed concentration range was 4×10^{-6}-10^{-2}M ,the slope of 50.7 mV/decade with correlation coefficient 0.9994 and detection limit equals to 2.5×10^{-6}M, life time was 52 days. From these results showed that the electrode was successfully applied to the determination of chloropromazine hydrochloride in pharmaceutical preparation.

Key Words: Chloropromazine hydrochloride selective electrode, chloropromazine hydrochloride determination, sodium tetra phenyl borate, plasticizers.

Introduction

Ion- selective electrodes (ISEs) are one of the most frequently used potentiometric sensors in laboratory analysis as well as in industry, process control, physiological measurements, environmental monitoring and drug analysis. Chloropromazine hydrochloride, N- [3- (2- chlorophenothiazine – 10 – yl) -N, N- dimethylamimonohydrochloride, $C_{17}H_{19}Cl N_2S.HCl$, is a white powder with moleculr weight 355.3gm/mole used commonly in the treatment of antipsychotic[1]. The most common method used in chloropromazine hydrochloride determination is spectrophotometer [2,3,4].An original,simple and sensitive flow-injection spectroanalytical method for the determinationof chloropromazine hydrochloride in pure form in pharmaceutical formulations was described by Daniela-Daniel [5]. The voltammetric behavior of antipsychotic drugs,such as, chloropromazine hydrochlorid, promothazine hydrochloride has been investigated at a glassy carbon electrode in Britton-Robinson buffer 9,it was found by applying differential pulse stripping (DPSV)that both chloropromazine hydrochloride and promethiazine hydrochloride has well formed oxidation voltammetic waves, with the peak potential for promethiazine hydrochloride at 620mV,and two peaks of chloropromazine hydrochloride at 444 and 668mV.The linear ranges for chloropromazine hydrochloride in the concentrations were of 0.05-1.2 and 0.1- 1mg\L respectively[6].Chloropromazine hydrochloride (CPH) could react with potassium ferrioxalate (PF) to form 3:1 ion association complexes ,which has been developed by Lanxiaing An[7].A speed and accurate titration method for the determination of (1-100) mg\L iron(II) as pure solutions and in its dosage forms was investigated and found to offer an improvement in ease.This method based on the direct visual titration of Iron (II) with ceric ammonium sulphate and employs chloropromazine hydrochloride in a mixture of sulphuric and phosphoric acids as a redox indicator[8]. Although L-ascorbic acid was determined by titration method, the rapid procedure was based on the direct visual titration of L-ascorbic acid with ceric ammonium sulphate in the presence of chloropromazine hydrochloride in a mixture of sulphuric and phosphoric acids as a redox indicator[9].A flow-injection coulometric method for the determination of chloropromazine hydrochloride on ion transfer into a plasticizer poly vinyl chloride (PVC) membrane, was developed,the detector used consists of a flow-through cell that incorporates a plasticized poly vinyl chloride (PVC) membrane which contains tetrabuty lammonium tetraphen ylborate as supporting electrolyte. A linear relation was observed between the quantity of electricity and chloropromazine concentrations over a range of 1 $\times10^{-6}$ 10^{-4}M,detection limit was 2×10^{-2}M [10]. Novel clozapine ion selective electrode was prepared with ion pair complex: Clozapine - phosphotungstate as electroactive material in PVC matrix membrane and dioctylsebacate as solvent mediator[11]. Several plasticize poly(vinyl chloride) (PVC) membranes of different compositions were tested for use in the construction of an ion -selective electrode for the determination of some multidrug resistance reverses. A membrane with a 1:2(w/w) 2-nitro phenyl octyl ether to PVC ratio, doped with 1%(w/w) tetrabutylamonium tetraphenyl borate was selected. A linear relation between potential and log C was obtained between 1×10^{-5} and 1×10^{-2} mol l^{-1} chloropromazine ,clomipramine ,imipramine, desipramine and verapamil with almost Nernstian response[12].Plasticized poly (vinyl chloride) ,PVC, with different membrane compositions tasted for use in the construction of an ion –selective sensor for the determination dibucaine,a prepared membrane with dioctylphthalate -PVC and ion-pair of N-preparedas a potentiometric sensor for the analysis of dibucaine [13].A novel ritodrine hydrochloride ion-selective PVCmembrane electrode based on ion –pair complex of ritodrine -tetra phenyl borate was prepared with di n-butyl phosphate as aplasticizer [14] .Atenolol selective electrodes were prepared based on a complex atenolol-phosphotungstate as an active material using the plasticizers di-buty phosphate (DBP) ,tri-butyl phosphate(TBP),o-nitro phenyl octyl ether (NPOE)and di-octyl phthalate (DOPH) in a PVC matrix membrane[15].Two simple assay procedures for quantitation of dothiepin HCl as been developed using dothiepin -selective electrode. The first electrodeI was based on drug, favianic acid ion pair complex,Bis(2-ethylhexyl-phthalate)and poly vinyl chloride (PVC) matrix ,second electrodeII based on drug tungstosilicicacd acid,Bis (2-etheylhexyl sebactate) as plasticizer and poly vinyl chloride matrix[16].A novel PVC membrane sensor for bisacodyl based on bisacody -phosphotungstate ion pair complex was prepared[17].The construction and electrochemical response characteristics of a poly (vinyl chloride) PVC membrane selective electrode for the determination of sulpiride (SPD) are described, the sensing membrane comprised an ion-exchange formed between the protonated drug and tetra phenyl borate (TPB) in a plasticized PVC matrix[18].

Experimental part

Equipment

1-Microprocessor based Bench pH/mV/C Meter, HANA Instruments,pH211,Made in Romania.

2-pH Electrode Type: HANA Instruments,H11131.

3-Calomel Reference Electrode Type: Gallen Kamp (USA).

4- The electrode used for chloropromazine hydrochloride was home constructed according to this method in reference [19],as follows: The Ag/Agcl electrode and 0.1M chloropromazine hydrochloride solution were used as the internal reference electrodeis shown in Figure 1, and the internal filling solution of the electrode respectively .One side of apiece of PVC tube (1-2cm long)was flattened and smoothed by placing it on glass plate moistened with THF.A disk of the membrane was cut equal to the external diameter of the PVC tubing and mounted on the polished end. The other side of the PVC tubing was then connected to the electrode body. The assembled electrodes were conditioned by soaking in 0.1M chloropromazine hydrochloride solution for at least 3h before the use of the electrodes.

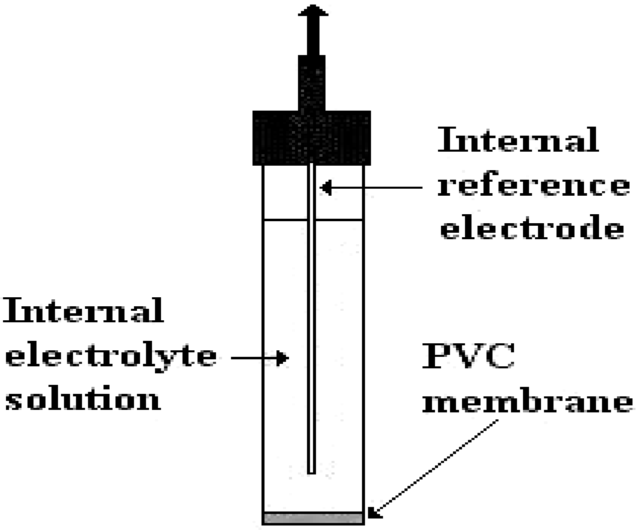

Figure 1:Electrode structure

Chemicals

1- Chloropromazine hydrochloride was obtained from the State Company Of Drug Industries and Medical Appliances (Samara-Iraq-SDI). Largactiel tablet 100mg (Opry Company for Drug Industrial (Syria-Aleppo) under the licience Co. events company-France.

2- Plasticizers: Di-n-butyl Phthalate (DBPH)98%,O-Nitro phenyl octyl ether (o-NPOE) 98% were obtained from Fluka AG,(Switzerland).

3-Poly vinyl chloride, Breon S110/10 B.P chemical U.K. Ltd.

4 -All chemicals were of analytical reagent grade and distilled water was used throughout. Standard Solution

5-standar solutions of chloropromazine hydrochloride were prepared by sub sequent dilution of 0.01 M stock solution which was obtained by dissolving 0.355gm of chloropromazine hydrochloride in 100 ml.

6-The effect of pH was examined using 0.1M hydrochloric acid and 0.1M sodium hydroxide.

7- Stock solutions 0.01M of each of NaCl, KCl, $MgCl_2$, $ZnCl_2$, $FeCl_3$, $CrCl_3$. were prepared and other standard solutions were prepared by subsequent dilution of the stock solutions .All solutions were prepared using distilled water

Preparation of electroactive materials

The chloropromazine hydrochloride-sodium tetra phenyl borate(CPH-NaTPB) was used as the electoactive material in the membrane. It was prepared by dissolving 0.342gm of sodium tetra phenyl borate in 100ml of water and mixing with100ml of 0.01M chloropromazine hydrochloride solution .The resulting white precipitate was filtered off, washed with water, and dried at room temperature.

Preparation of the electrode

The mixture of the PVC was prepared by dissolved 0.04gm of chloropromazine hydrochloride –sodium tetra phenyl borate,0.17 gm of high molecular weight Poly vinyl chloride,0.36gm of DBPH and o-NPOE in 6-7ml of tetrahydrofuran with stirring to homogeneity 20].The mixture was poured into a glass ring (30-35mm diameter) resting on a glass plate, and a pad of filter was placed on top of the glass. The solvent was then allowed to evaporate at room temperature over about 2days. The thickness of the membrane obtained was about 0.5mm.

Results and Discussion

The performances of the electrodes prepared with the ion-pair complex chloropromazine hydrochloride-sodium tetra phenyl borate as an electroactive material in the membrane were studied The results of electrode parameters obtained from the calibration graphs are listed in Table.1with Figure2.and Figure 3.

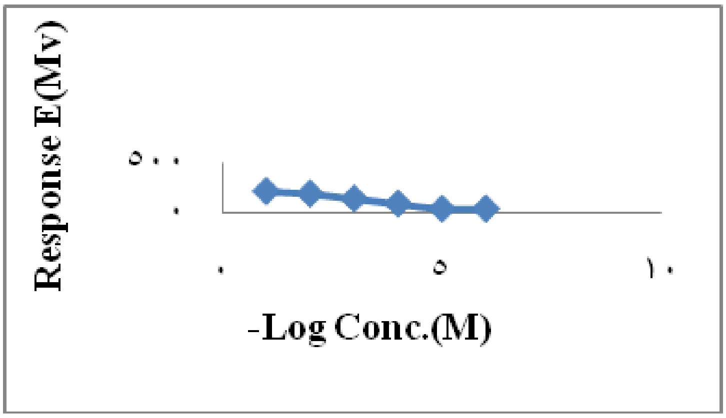

Figure 2:Calibration curve of Chloropromazine hydrochloride selective electrode based on (CPH-NaTPB)ionophore and DBPH plasticizer

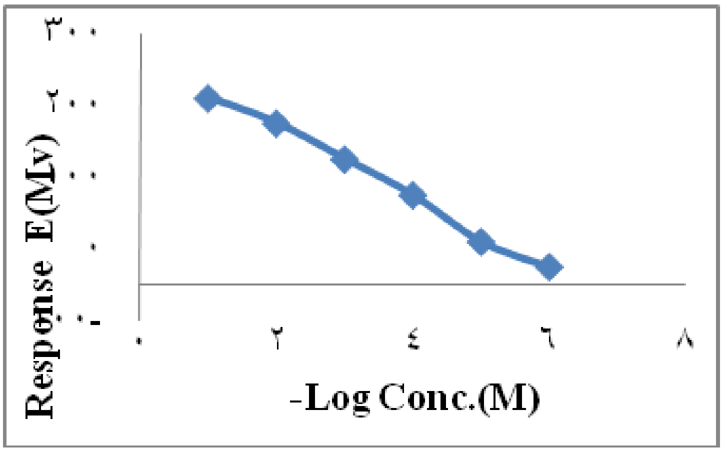

Figure 3:Calibration curve of Chloropromazine hydrochloride selective electrode based on (CPH-NaTPB)ionophore and NPOE plasticizer.

Table1.Characteristics of the chloropromazine hydrochloride electrodes.

Membrane no.	I	II
Plasticizer	DBPH	O-NPOE
Slope (mv/decade)	54.1	50.7
Correlation coefficient	0.9996	0.9994
Linear range(M)	5×10^{-4}-10^{-2}	4×10^{-6}-10^{-2}
Detection limit(M)	2×10^{-4}	2.5×10^{-6}
Lifetime (day)	72	52

To compared the result between electrode (I) (CPH+ Na- TPB + DBPH) and electrode (II) (CPH+Na-TPB +NPOE) the slope of these electrodes were near to Nernstain slope and the correlation coefficients were near to one, the lifetime of electrode (I) was relatively longer than life time of electrode (II) ,this means the electrode (I) based on DBPH can be used for 72 days,after this time the electrode(I)becomes less sensitive toward chloropromazine hydrochloride which may be due to gradually leaching the sensor from the membranes to the external solution.

Effect of pH

The effect of pH on the response of the electrodes was examined by measuring the potential variation over the pH range from 1.0 to 11.5 for 2different chloropromazine concentration 1.00×10^{-3}M and 1.00×10^{-2}M.The working PH ranges for the electrodes are listed in Table 2.

Table 2:Working pH range for chloropromazine hydrochloride electrodes at different

	pH	
Membrane no.	Conc. Of CPH 1.00 $\times10^{-2}$ M	Conc. Of CPH 1.00 $\times10^{-3}$M
I	3.9-11	4.2-10.6
II	4.2-7.1	4.4-7

concentration of chloropromazine hydrochloride solution.

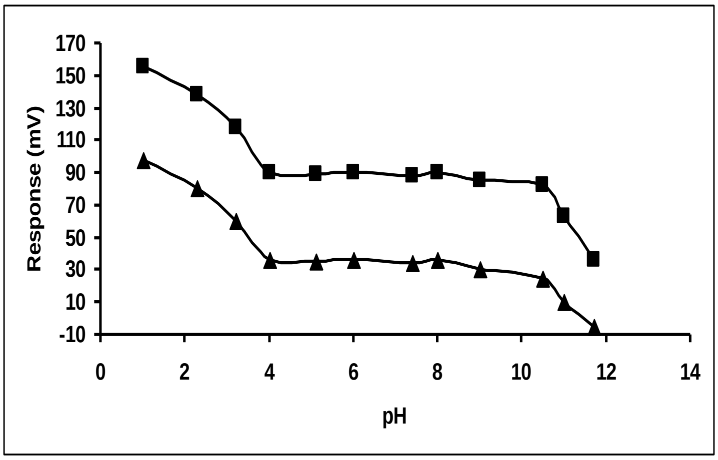

Figure 4: Effect of pH response of the electrode I at different(CPH) concentrations
■ -10^{-2} M,♦-10^{-3} M based on DBPH

A typical plot for the pH effect on chloropromazine hydrochloride electrodes based on DBPH plasticizer is shown in Figure 4 . The pH was adjusted with sodium hydroxide and hydrochloric acid solutions It can be seen that the potential does not change over a wide pH range;therefore,the proposed electrodes can be used for measuring awide range of chloropromazine hydrochloride concentrations. However, outside this range the electrodes responses change. That is at pH values higher than 11.5,the potential gradually decreased, which may be attributed to the poisoning the membrane by formation a white precipitate of sodium tetra phenyl borate oxides.At pH lower than 1.0(very high acidity)the electrodes response has been increased irregulary; this may be due to that the electrodes response to H^+ activities as well as analyte ions.

Response time

The electrode response time to reach a potential within ±2mv of the final equilibrium value was determined. The measured response time for chloropromazine hydrochloride electrode based on DPBH for 0.01M chloropromazine hydrochloride solution was 7.4 and 5.8 s for 1.00×10^{-4}M chloropromazine hydrochloride solution, while for the electrode based on NPOE plasticizer the response time was 7.7 and 5.8s for 0.01 and 1.00×10^{-4}M chloropromazine hydrochloride solution,respectively.

Effect of temperature of the test solution

To study the effect of temperature,the electrode potential of 10^{-6}-10^{-2} M drug solutions were determined in 25,30,35,40^{0}C.A different temperature were gave different value of slope is reported in Table 3.

Table3: Performance characteristics of CPH-selective electrode at different temperatures.

mV/decade	Temp.0C	Membrane no
54.1	25	I
66.8	30	
79.2	35	
100.0	40	
50.7	25	II
65.6	30	
73.9	35	
98.6	40	

From Table 3 ,it is obvious that the electrode gave a good Nernstian response in the temperature range 25-30^{0}C,the slope of electrode jump to a very high value(100.0 and98 mVdecade^{-1} respectively) at 40^{0}C which may be attributed to decomposition of the ion pair.

Selectivity

E_A and E_B ,z_A and z_B ,a_A and a_B are the potentials, charge numbers and activities for the primary and interfering ions, respectively, and a_A =a_B =0.01 M

Table 4:Selectivity coefficient for CPH electrode based on DBPH plasticizer.

Conc.ofCPH (M)	**K $_{A,B}$ for Ion interfering**					
	Na^+	K^+	Mg^{2+}	Zn^{2+}	Fe^{3+}	Cr^{3+}
0.1	$8.9 *10^{-6}$	$6.9*10^{-6}$	$2.3*10^{-6}$	$1.7*10^{-6}$	$1.1*10^{-5}$	$7.9*10^{7}$
0.01	$7.9*10^{-6}$	$6.9*10^{-6}$	$6.9*10^{-7}$	$4.9*10^{-7}$	$2.9*10^{-6}$	$1.8*10^{-}$
0.001	$1.9 *10^{-5}$	$1.6*10^{-5}$	$4.7*10^{-7}$	$5.9*10^{-7}$	$3.1*10^{-6}$	$1.4*10^{7}$
0.0001	$5.4*10^{-5}$	$4.9*10^{-5}$	$4.9*10^{-7}$	$5.8*10^{-7}$	$4.9*10^{-6}$	$1.8*10^{7}$
0.00001	6.23	$3.5*10^{-3}$	$1.1*10^{-5}$	$2.6*10^{-5}$	$5.8*10^{-6}$	$1.8*10^{-}$

Table 5:Selectivity coefficient for CPH electrode based on NPOE plasticizer.

Conc.of CPH (M)	K $_{A,B}$ for Ion interfering					
	Na^+	K^+	Mg^{2+}	Zn^{2+}	Fe^{3+}	Cr^{3+}
0.1	$1.1 *10^{-5}$	$5.2*10^{-6}$	$9.1*10^{-7}$	$1.1*10^{-6}$	$2.2*10^{-6}$	$1.2*10^{-6}$
0.01	$2.2*10^{-5}$	$7.1*10^{-6}$	$6.5*10^{-7}$	$6.8*10^{-7}$	$5.3*10^{-7}$	$6.9*10^{-7}$
0.001	$6.6 *10^{-5}$	$3.3*10^{-5}$	$2.5*10^{-6}$	$1.6*10^{-7}$	$5.8*10^{-7}$	$7.2*10^{-7}$
0.0001	$3.5*10^{-5}$	$3.3*10^{-5}$	$3.1*10^{-7}$	$5.8*10^{-7}$	$1.8*10^{-7}$	$1.0*10^{-6}$
0.00001	$3.9*10^{-3}$	$3.5*10^{-4}$	$1.3*10^{-6}$	$1.3*10^{-6}$	$4.1*10^{-7}$	$2.2*10^{-6}$

The selectivity coefficient values indicate good selectivity for chloropromazine hydrochloride against alkali, alkaline earth and some common transition metal ions,the selectivity coefficient for monovalent ions is higher than that for divalent and trivalant. This may be due to the differences in ionic size, mobility and permeabilityGenerally, the values of selectivity coefficient in the above tables indicated that the interference was increased as the concentration of the drug decrease. Also the higher interference was noticed for mono valent cations than di and tri-valent cations. The higher interference of cations at concentration 10^{-5}M show in Table 4 is due to the electrode sluggish response to the drug at low concentrations. In this case the drug starts to leach from the membrane to the external solutions which contains the interfering cations and the cations can be exchanged to the drug of the complex in the membrane. Therefore, the interference of the cations on electrode response may be increased.

Analysis Sample

The concentration of chloropromazine hydrochloride in prepared standard solutions were determined using an electrodes based on DBPH and NPOE. Four potentiometric techniques were used for the determination of chloropromazine hydrochloride, namel direct measurement, single standard additions(SA),multi-standard addition (MSA)and titration as shown in Figure5 and 6. Standard solution of chloropromazine hydrochloride with a concentration of 1.00×10^{-3} M was used in SA and 1.00×10^{-3}M of sodium tetra phenyl borate used as the titrant for the titration. The results of the quantitative measurements for CPH solutions with relative standard deviations and relative error are listed in Table 6.

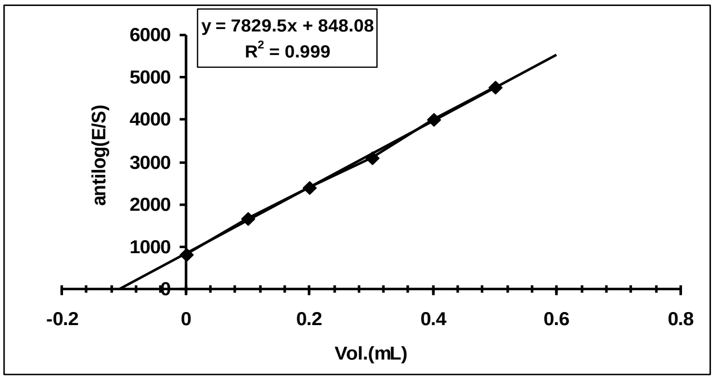

Figure 5:Antilog (E /S)versus volume of 10^{-3}M added of chloropromazinhdrochloride using electrode (I).

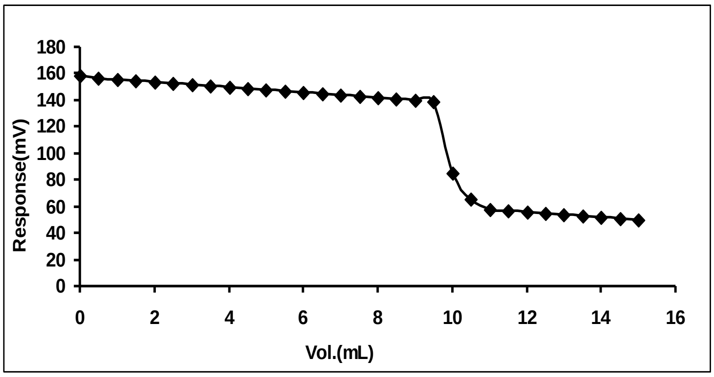

Figure 6:Titration curve for sample 10^{-3}M(CPH)with 10^{-3}M(Na-TPB)standard by electrode(I).

Table 6 shows that the electrode (I) (CPH-NaTPB +DBPH)

Electrode No.	**Concentrations (M)**				
	Sample	**Measurements using potentiometric methods**			
		Direct	**SA**	**MSA**	**Titration**
I	1×10^{-3}	1.010×10^{-3}	1.004×10^{-3}	1.001×10^{-3}	0.98×10^{-3}
	RSD%	1.104*	0.679*	-	2.368*
	RC%	101.0	100.4	100.1	98
	RE%	1	0.4	0.1	-2
II	1×10^{-3}	1.031×10^{-3}	0.99×10^{-3}	1.003×10^{-3}	0.96×10^{-3}
	RSD%	1.534*	1.048*	-	2.741*
	RC%	103.1	99	100.3	96
	RE%	3.1	-1	0.3	-4

* Each measurement was repeated three times.

Table 6 shows that the electrode (I) (CPH-NaTPB +DBPH) gave better results than the electrode (II) (CPH-Na-TPB+NPOE) because the relative standard deviation (RSD%) of electrodeII for concentration 10^{-3} M was1.048 ,1.534and 2.741 respectively,this means the precision of the electrode (I) using direct method is better than the electrode(II),it may be the low slope of electrode (II),also the relative standard deviation(RSD%) for electrode(I) was much lower than the relative standard deviation for electrode (II) in (SA) ,(MSA) and titration methods. The relative error obtained from (SA)and (MSA) methods for electrode (I) are 0.4,0.1,-2respectively and for electrode (II) the relative error are-1 ,0.3,-4 respectively,this consistent with the properties of standard addition method which the influence of the interferences to be eliminated.

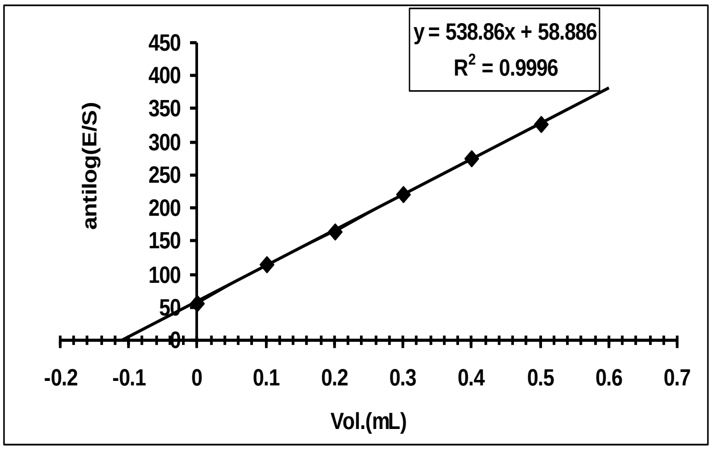

Figure 7:Antilog (E /S)versus volume of 10^{-3}M added of Largactiel using electrode (I).

Table 7: Largactiel tablets analyses for electrode(I) and electrode (II).

Electrode No.	**Concentration(M)**				
	Sample	**Measured using potentiometric methods**			
		Direct	SA	MSA	Titration
I	1×10^{-3}	1.021×10^{-3}	0.992×10^{-3}	0.998×10^{-3}	0.97×10^{-3}
	RSD%	1.431^{*}	0.977^{*}	-	2.578^{*}
	RC%	102.1	99.2	99.8	97
	RE%	2.1	-0.8	-0.2	-3
II	1×10^{-3}	0.97×10^{-3}	0.986×10^{-3}	1.007×10^{-3}	0.95×10^{-3}
	RSD%	1.618^{*}	1.053^{*}	-	2.965^{*}
	RC%	97	98.6	100.7	95
	RE%	-3	-1.4	0.7	-5

* Each measurement was repeated three times

Table 7 shows that the the electrode (I) gave better results than electrode (II) in the SA method, the tablets of chloropromazine hydrochloride in Largactiel drug because the electrode (I) have(RSD%) about0.977,that means have good precision than electrode (II) in which (RSD%) equal 1.053.The relative error(RE%) for (SA), (MSA)and titration methods are ,-0.8,-0.2,-3 respectively for electrode (I) compared with electrode (II) are 1.4,0.7,-5 respectively, which are good results for Largactiel drug compared with electrode (II) because the electrode (II) gave lower slope than electrode (I).

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بناء ودراسة خواص اقطاب الكلوروبرومازين هيدروكلورايد الانتقائية المستندة على معقد كلوروبرمازين هيدروكلورايد– صوديوم رباعي فنيل بوريت في مادة متعدد كلوريد الفينايل.

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الملخص

صنعت اقطاب الكلوروبرومازين الانتقائية الايونية بالاعتماد على معقد كلوروبرومازين– صوديوم رباعي فنيل بوريت كمادة فعالة باستخدام المواد الملدنة di- butyl phthalate DBPH و o-nitro phenyl octyl ether NPOE في مادة متعدد فينايل كلوريد PVC.تم دراسة خواص الاقطاب المحضرة.فبالنسبة للقطب المستند على DBPH كمادة ملدنة .فقد تم الحصول على مدى تركيزي تراوح من 5×10^{-4} M الى 10^{-2} M وميل نيرنيستي بمقدار 54.1mV/decade وبمعامل ارتباط 0.9996 .حد التحسس كان بمقدار 2×10^{-4}M وعمر القطب بمقدار 72 يوما.اما عن قطب NPOE فقد تم الحصول على مدى تركيزي بحدود 4×10^{-6}-10^{-2}M وميل بمقدار 50.7mV/decade ومعامل ارتباط 0.9994 وحد تحسس مساوي ل 2.5×10^{-6} M وعمر القطب 52يوما . أظهرت النتائج المستحصلة امكانية استخدام القطب بنجاح في تقدير الكلوروبرومازين في أقراص الادوية المحضرة.