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Research Article

CONSTRUCTION AND POTENTIOMETRIC STUDY OF CIPROFLOXACIN SELECTIVE ELECTRODES

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ABSTRACT

Three ciprofloxacin hydrochloride selective electrodes(CFH) were described ion pair was ciprofloxacin hydrochloride(CFH)–Molybdophosphoric acid (MPA),with di-butyl butyl phthalate (DBPH), tri-butyl phosphate(TBP) and o-nitro phenyl octyl ether(o-NPOE) as a plasticizers, and these electrodes were gave slope near to 53.30 , 43.40, 50.10 mV/ decade, respectively with concentration range from 4.0×10^{-6} to 1.0×10^{-1} M , 2.5×10^{-4} -1.0×10^{-2}M, and 6.1×10^{-6} -1.0×10^{-1}M, ,respectively, detection limit was 1.2×10^{-6}, 2.5×10^{-5},and 2.3×10^{-6} M, respectively, Correlation coefficients were near to 0.9998, 0.9990, 0.9998, ,life time was around to8,2, 1 week, respectively, and were studied PH effect, selectivity, potentiometric method for pharmaceutical preparations.

Keywords: Ciprofloxacin, Selective electrodes, Sensors.

INTRODUCTION

Ciprofloxacin (1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid, it used to treatment as antibacterial[1],shown in Fig.1

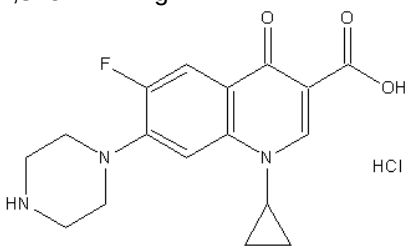

Fig. 1: Chemical Structure of ciprofloxacin hydrochloride

To determination ciprofloxacin hydrochloride, four spectrophotometric methods were described,the range of concentration was 5-50,1.5-15 and 20-200µg ml^{-1} of(CFH) with relative standard deviation equel to 1.5%[2],concentration range was about 20-250 ng /ml with r^2 = 0.9993[3],linear range was from 2.0-7.0 µg ml^{-1} with relative standard deviation from 1.55 to 2.47%(n=6)[4],concentration rang was 0.5-3.5 µg ml^{-15}.High performance liquid chromatography has been developed by using C-18 column,flow rate was 2.0 ml / min[6],concentration range was 100 to 600 ng $spot^{-1}$ [7].Spectroscopic method proposed for ciprofloxacin hydrochloride by fourier transform infrared,the carbonyl group centered at 1707 m^{-1} at PH equal to 6.0[8].P-25 TiO_2 photocatalyst as artificial radiation was investigated of ciprofloxacin hydrochloride(CFH),minimum rate of degradation occurs at PH=9[9].To novel zinc(ll) complexes with ciprofloxacin and determined by element analysis, IR spectroscopy, mass spectrometry,TG analysis[10].Two types of ciprofloxacin membrane potentiometric sensor were made by used ciprofloxacin – tetraphenyl borate as an ion pair at membrane configuration of 20% ion pair and5% ion pair , 65%DBP 30% PVC, 5%MWCNTs 55%graphit, 20%IL[11].Ciprofloxacine - selective electrodes were examined by used sodium tetraphenylborate (Na-TPB), phosphotungstate (PTA), and

phosphomolybdate (PMA),with di-butyl phosphate as a plasticizer.These electrodes were gave Nernstian slopes: 58.3,57.7,51,7,50.7,44 and 41.8 mV/decade[12].

MATERIALS AND METHODS

Chemicals

1. Ciprofloxacin hydrochloride were supplied from Drug Industries and State Company of(SamaraIRAQ-SDI) , and Medical Appliances.
2. Ciropharm(500 mg),Mfg.by pharma International Co.Amman- Jordan.
3. Chemical PVC from U.K.Ltd,Breon S110/10 B.P.
4. THF was from(BDH).
5. Plasticizers: di-butyl phthalate (DBPH),tri-butyl phosphate(TBP) and o-nitro phenyl octyl ether(o-NPOE), were from Fluka AG.
6. Supplementary all chemicals materials of analytical were provided from Fluka,Aldrich and BDH.

Equipment

1-HANA Instruments,pH 211,Made in Romania,Microprocessor , pH/mV/C Meter.
2- Reference Electrode Type: Calomel(Gallen Kamp)(USA).
3- HANA Instruments,H11131 as pH Electrode .
4-0.1 M of ciprofloxacin hydrochloride solution was used as an internal solution with Ag /AgCl wire.

Standard Solutions

1-0.1 M of ciprofloxacin hydrochloride standard solution was organized and the other concentration were set as succeeding by attenuation from stockpile solutions.
2-Solutions used to measure the selectivity equipped from 0.01M of stock solutions of NaCl,KCl.$MgCl_2$,$ZnCl_2$,$FeCl_3$,and $AlCl_3$ and dilution by successive with used distilled water.

Ion –pair (CFH-MPA) preparation

Ion – pair (CFH-MAP) was equipped by mingling 50 ml of ciprofloxacin hydrochloride solution which was have concentration 0.01 M with molybdophosphoric acid solution was have concentration 0.01M by thrilling .The result was filtered and clean by washing with distilled water, at that time dehydrated at room temperature.

PVC Membrane Electrode

PVC membrane detecting was equipped by mingling 0.04 gm of the (CFH-MPA) with 0.17 gm of great molecular weight PVC and 0.36 gm of the plasticizer (DOPH, TBP, o-NPOE) .Afterward homogenization, 6-7 mL of THF was supplemented and agitated. The blend was dispensed in 5 cm in diameter glass circle and permitted to vaporize for 24 hours.Main membranes with thickness of 0.10 mm were achieved and used for the erection of the electrodes.

RESULT AND ARGUMENT

The accomplishments of ciprofloxacin electrodes organized with complex: ciprofloxacine hydrochloride-molybdophosphoric acid (CFH-MPA) as an energetic substantial in the membrane were empirically matched.From the gradation diagrams which recorded in Table 1,the consequences of electrode parameters attained.A little slopes prices achieved for membrane (CFH-TBP-MPA) might be ascribed to the plasticizer was used, TBP,which enclosed a lengthy alkyl chain committed to the group of phosphate,which might lessening of ion exchange method stuck between the exterior solution of ciprofloxacin and the electroactive(CFH-MPA)[13].Potential reply for suggested electrode (CFH-DBPH-MPA) by changing concentrations of ciprofloxacin was donated a slope of 53.30 mV/decade,lifetime of around 8weeks,detection limit was 1.2×10^{-6} M were recorded in Table.1.On the other hand electrode (CFH-NPOE-MPA), was donated a slope of 50.10 mV/decade, lifetime near to 1weeks, this could be ascribed to the irreconcilability of NPOE with the complex (CFH-MPA), producing a filtering of the compound out of membrane to the exterior solutio[14].Calibration graph for the ciprofloxacin electrodes was shown in diagrams 1,2,3,4 for electrode (CFH-DBPH-MPA) and (CFH-NPOE-MPA),respectively. The permanence of the two electrodes was examined constantly by using concentration 1.00×10^{-3} M of ciprofloxacin solution with appraised diurnal.

Table 1: Response of Ciprofloxacin hydrochloride electrodes(CFH-MPA)

Type.of membrane	CFH+DBPH+MPA	CFH+TBP+MPA	CFH+NPOE+MPA
Concentration range/M	4.0×10^{-6} -1.0×10^{-1}	2.5×10^{-4}- 1.0×10^{-2}	6.1×10^{-6} -1.0×10^{-1}
Correlation coefficient(R)	0.9998	0.9990	0.9998
Detection limit/M	1.2×10^{-6}	2.5×10^{-5}	2.3×10^{-6}
Slope mV/decade	53.30	43.40	50.10
Lifetime /week	8	1	2

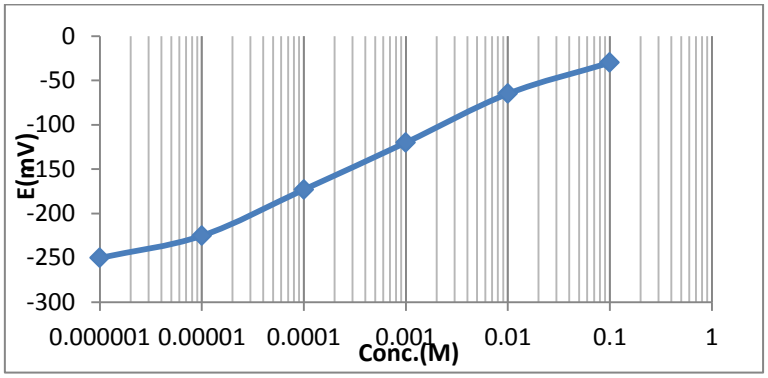

Diagram. 1: Response of Electrode based on(CFH-DBPH-MPA)

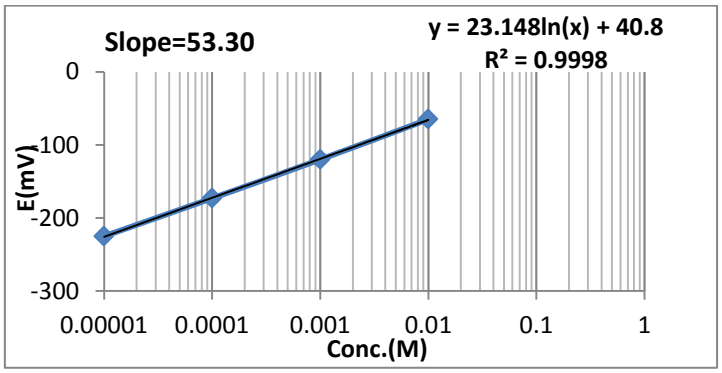

Diagram. 2: Calibration graph of Electrode(CFH-DBPH-MPA)

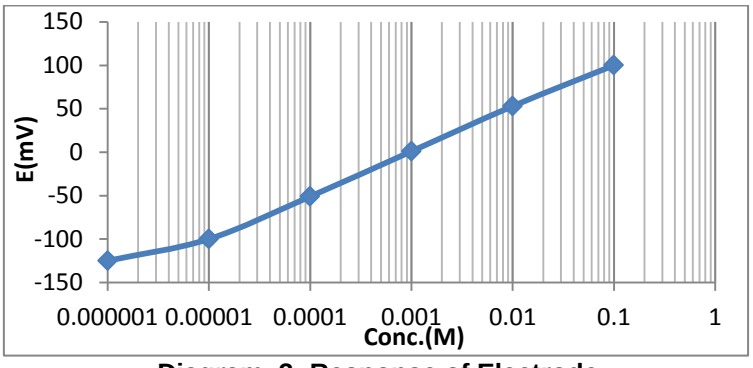

Diagram. 3: Response of Electrode based on (CFH-NPOE-MPA)

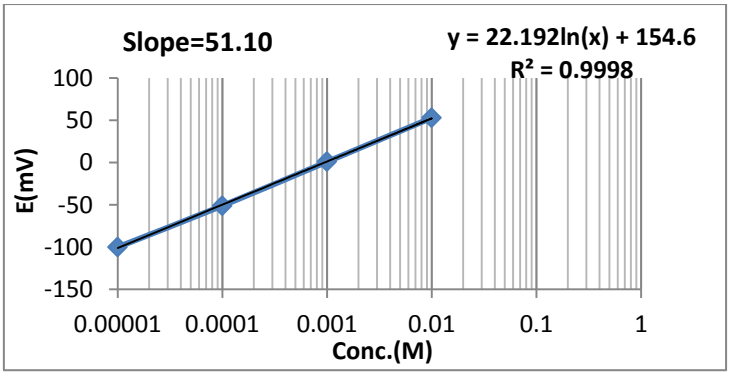

Diagram. 4: Calibration graph of Electrode(CFH-NPOE-MPA)

Effect of pH

PH effect of ciprofloxacin hydrochloride deliberate by verifying the difference potential for 1.00 x 10^{-3}M concentrations of drug.Diagram 5 shown The functioning of PH of electrodes are recorded in Table 2.

Table 2: Range of PH for ciprofloxacine electrodes

Electrode's Type	pH range
DBPH+CFH+MPA	3.5-6.0
TBP+CFH+MPA	4.5-6.8
NPOE+CFH+MPA	3.0-7.5

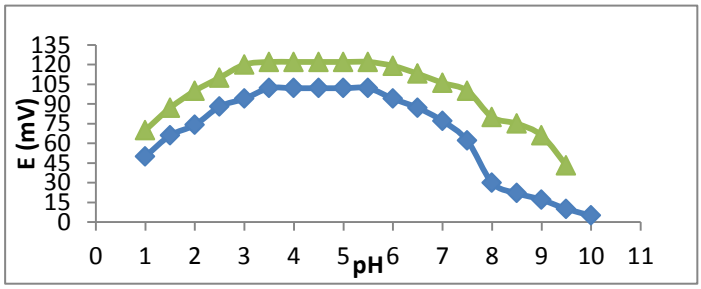

Diagram. 5: PH response of Electrode (DBPH+CFH+MPA) at two concentration for ciprofloxacin hydrochloride solution,▲10^{-3}M,■10^{-4}M

pH was modified by way of hydrochloric acid and sodium hydroxide solutions. The perceived drifts on upper pH measurements possibly will be due to the construction of sodium phosphate or molybdate oxide.

Selectivity

Selectivity coefficient measurement by using separate solution method ,and was deliberate affording to the equation:[15]

$\log K^{pot}_{A,B} = [(EB – EA) / (2.303 RT/zAF)] + (1 – zA/ zB) \log aA$

numbers charge were zA,zB, potentials were EA and EB, activities for the major and intrusive ions were aAand aB, ,and aA= aB= 0.01M.

Values of the selectivity coefficient for ciprofloxacin electrodes depened on NPOE and DBPH for Various Mono-valent ,Di-valent and Tri-valent are recorded in Table 3.and selectivity of (CFH+MP+DBPH) electrode for interfering Mg^{2+} by separation method was shown in Diagram.6

Table 3: Separate solution method(1×10^{-3} M of CFH and the interference)for determination Selectivity coefficient

Interfering Ion	$K^{POT}_{A,B}$ for electrode DBPH+CFH+MPA	$K^{POT}_{A,B}$ for electrode NPOE+CFH+MPA
Na^{+1}	10^{-4} 1.5780×	9.2357×10^{-4}
K^{+1}	1.426×10^{-3}	2.0902×10^{-4}
Mg^{+2}	2.7314×10^{-5}	2.7314×10^{-5}
Zn^{+2}	1.0465×10^{-6}	1.8033×10^{-4}
Fe^{+3}	1.13431×10^{-6}	8.0140×10^{-4}
Al^{+3}	9.7757×10^{-3}	9.775×10^{-3}

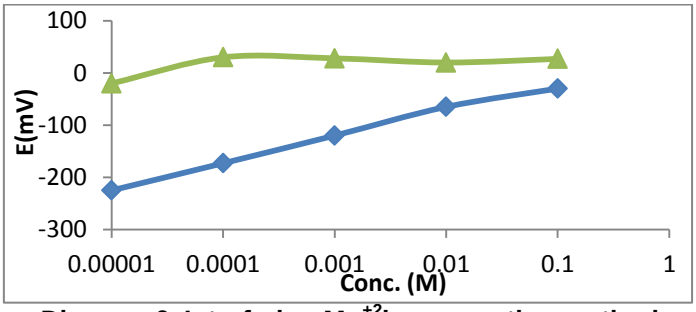

Diagram 6. Interfering $Mg^{+2}$by separation method for (CFH+ DBPH +MPA) membrane, ♦ –ciprofloxacin hydrochloride solution, ▲ ⁻ solution of Mg^{+2}

Selectivity coefficients showed good values for ciprofloxacin electrodes hydrochloride versus alkali, alkaline earthand a number of corporate alteration metal ions. Additionally, the selectivity coefficient for mono-valent,di-valent,tri-valent ions were less than 0.1thus,with several interferings ions no interference.

Sample Analysis

For the determination of ciprofloxacin hydrochloride, potentiometric performances were used these comprised titration method, direct method, standard addition method (SAM) and multi standard addition method,were shown in diagram 7,8,9,10.Potentiometric titration of 10^{-3} M Molybdophosphoric acid(MPA) were used as a titrant.A emblematic titration scheme was presented in diagram 11.The products of sample analysis are recorded in Table (4),(5).

Table 4:Potentiometric techniques for analysis of ciprofloxacin HCl samples.

Electrode Type	Sample	Concentration(M) Response by potentiometric method			
		Direct	SAM	MSA	Titration
CFH+ DBPH+MPA	1×10^{-3}	0.9934×10^{-3}	0.9790×10^{-3}	0.9871×10^{-3}	0.9615×10^{-3}
	RSD%	0.4	1.3	-	-
	Re%	99.34	97.90	98.71	96.15
	Er%	- 0.6	- 2.1	- 1.2	-3.8
	1×10^{-4}	0.9875×10^{-4}	0.9488×10^{-4}	0.9754×10^{-4}	0.9835×10^{-4}
	RSD%	0.7	1.8	-	-
	Re%	98.75	94.88	97.54	98.35
	Er%	-1.2	-5.1	-2.4	-1.6
CFH+ NPOE+MPA	1×10^{-3}	0.9868×10^{-3}	0.9630×10^{-3}	0.9880×10^{-3}	0.9799×10^{-3}
	RSD%	0.3	2.7	-	-
	Re%	98.68	96.30	98.80	97.99
	Er%	-1.3	- 3.7	-1.2	-2.0
	1×10^{-4}	0.9855×10^{-4}	0.9788×10^{-4}	0.9678×10^{-4}	0.9773×10^{-4}
	RSD%	0.7	2.8	-	-
	Re%	98.55	97.88	96.78	97.73
	Er%	-1.4	-2.1	-3.2	-2.2

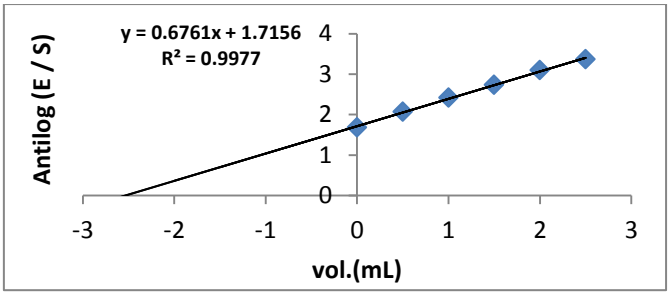

Diagram. 7:Plot of multi standard addition methods for determinationCFH by using electrode (CFH+ DBPH+MPA) with 10^{-4}M of ciprofloxacin hydrochloride solutions

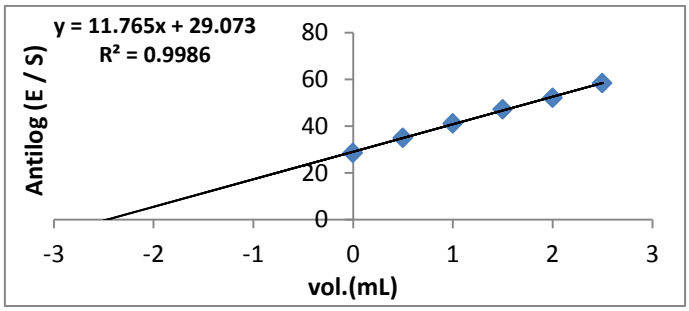

Diagram. 8:Plot of multi standard addition methods for determination CFH by using electrode (CFH+ NPOE+MPA) with 10^{-4}M of ciprofloxacin hydrochloride solutions

Table 5: Ciprofloxacin hydrochloride (Cipropharm) tablets analysis for electrode (CFH-DBPH+MPA) and electrode (CFH+NPOE+MPA)

Electrode No.	Concentration(M)				
	Sample	Response by potentiometric method			
		Direct	SAM	MSA	Titration
CFH+ DBPH+MPA	1×10^{-3}	0.9368×10^{-3}	0.9973×10^{-3}	0.9976×10^{-3}	0.9850×10^{-3}
	RSD%	1.5	1.4	-	-
	RE%	93.68	99.73	99.76	98.50
	Er%	6.3-	- 0.2	-0.2	- 1.5
CFH+ NPOE+MPA	1×10^{-3}	0.9452×10^{-3}	0.9962×10^{-3}	0.9984×10^{-3}	$\times10^{-3}$ 0.976
	RSD%	2.6	1.6	-	-
	RE%	94.52	99.62	99.84	97.60
	Er%	- 5.4	- 0.3	-0.1	- 2.4

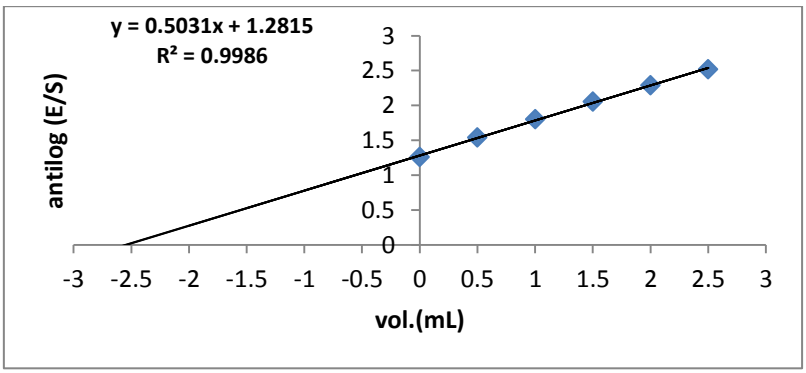

Diagram. 10: Plot of multi standard addition methods for determination CFH by using electrode (CFH+ DBPH+MPA) with 10^{-3}M of ciprofloxacin hydrochloride solutions in cipropharm tablets

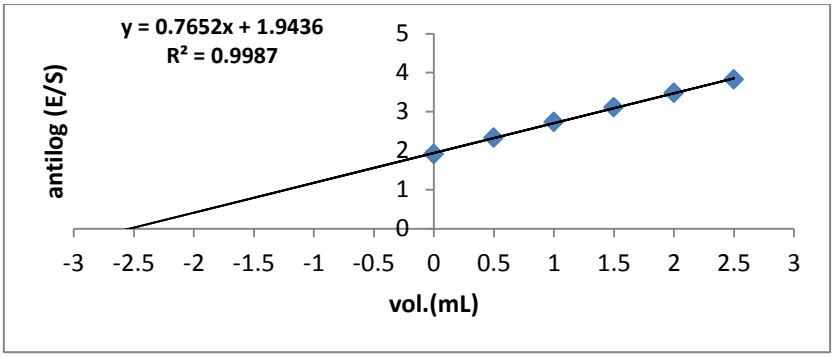

Diagram. 11: Plot of multi standard addition methods for determination CFH by using electrode (CFH+ NPOE+MPA) with 10^{-3}M of ciprofloxacin hydrochloride solutions in ciropharm tablets

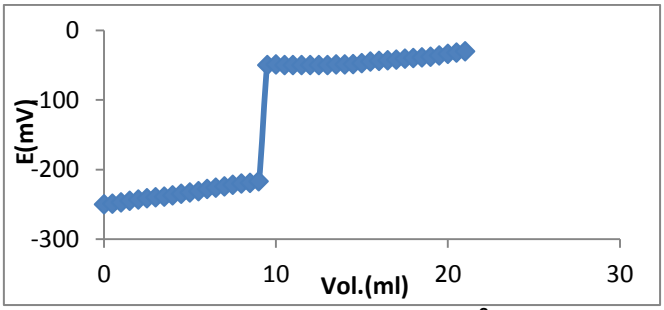

Diagram. 12: Titration curve for sample(1×10^{-3}M) CFH with(1×10^{-3}M) MPA standard by electrode(CFH+ DBPH+MPA)

CONCLUSION

In this work, Ciprofloxacin hydrochloride selective electrodes were construction based on PVC matrix with complex :(CFH-MPA) and with changed plasticizers.The best Ciprofloxacin electrode was depended on DBPH, which was used for determination the drug in pharmaceutical formulations.This electrode was gave excellent parameters,no interference with various cations. The suggested analytical method is verified to be easy and fast, with good accurateness.

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