Construction of New Ion Selective Electrodes for Determination Fe(III) and Their Application in Pharmaceutical samples

*Khaleda H. Al-Saidi** *Weaam R. Aziz**

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Abstract:

Liquid membrane electrodes for the determination iron(III) were constructed based on chloramphenicol sodium succinate and iron(III) CPSS-Fe(III) as ion pair complex, with four plasticizers Di-butyl phosphate (DBP); Di-butyl phthalate (DBPH); Di-octyl phthalate (DOP); Tri-butyl phosphate (TBP); in PVC matrix . These electrodes give Nernstian and sub-Nernstian slopes (19.79, 24.60, 16.01 and 13.82mV/decade) and linear ranges from ($1x10^{-5}$-$1x10^{-2}$ M, $1x10^{-5}$-$1x10^{-2}$ M, $1x10^{-6}$-$1x10^{-2}$ M and $1x10^{-5}$-$1x10^{-2}$ M) respectively. The best electrode was based on DBP plasticizer which gave a slope 19.79 mV/decade, correlation coefficient 0.9999, detection limit of 9×10^{-6} M, lifetime 37 day displayed good stability and reproducibility and used to determine iron(III) in pharmaceutical samples. The selectivity coefficient interferences of (K^+, Na^+, Cu^{+2}, Mn^{+2}, Zn^{2+}, Al^{3+},Folic acid) were studied using separate and mixed methods for selectivity coefficient determination. The pH and life time of the electrodes were also studied.

Key words: Iron(III) selective electrodes, Chloramphenicol sodium succinate.

Introduction:

Iron(Fe) is a naturally occurring magnet metal that attracts iron and steel. Its chemical symbol is (Fe) atomic weight 55.845 g/mole. Iron is one of the most common elements found in the earth's crust. It can be found in soils, sediments, water and in most living organisms. Iron is removed from the earth in the form of ores, which are processed and refined to obtain high-grade iron. Most iron ores are used in making iron and steel. These materials are used for building bridges, roads, ships and buildings. Iron is also used in dyes, water treatment, pigments for rubber and paints, and integrated circuits. It is also used as vitamins and supplements.[1]

Chloramphenicol sodium succinate (CPSS), a white or yellowish-white powder, hygroscopic, very soluble in water. Chloramphenicol sodium succinate has a molecular weight of 445.2 .it's empirical formula is $C_{15}H_{15}Cl_2N_2\ NaO_8$ and it's structural formula is show in fig (1).[2]

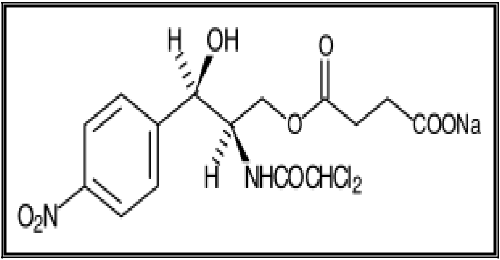

Fig. 1: Structure formula of Chloramphenicol sodium succinate.

Several methods for the determination of Fe(III) have been reported in the literature, including ion selective electrodes [3,4,5], spectrophotometric [6,7], liquid chromatographic[8] and derivatives

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*Chemistry Department, College of Science, Al-Nahrain University, Al-Jaderia, Baghdad, IRAQ spectrophotometry methods[9,10,11]. In this work the sensor is based on CPSS- Fe(III) as ion pair complex in polyvinyl chloride plasticized with DBP plasticizer was used for the determination Fe(III). The applications of ion selective electrodes continue to be of interest in pharmaceutical analysis because these sensors offer the advantages of simple design and operation, reasonable selectivity, fast response, low cost and applicability to turbid and colored solutions.

Materials and methods:

Equipment

An expandable ion analyzer (Orion model EA-940, USA), a pH meter (WTW model pH 522, Germany) and a silver-silver chloride electrode were used in this work.

Chemicals and reagents

High molecular weight poly vinyl chloride (PVC), (Breon S 110/10 B.P Chemical U. K. Ltd). Chloramphenicol sodium succinate (CPSS) standard from (Samara IRAQ-SDI). Ferric sulfate[$Fe_2 (SO_4)_3.9H_2O$] standard from (Fluka). Feroglobin capsules(24 mg iron+12mg zinc+2000 µg copper+500µg folic acid), made in (London- England). (DBP), (DBPH), (DOP) and (TBP) were purchased from Fluka AG, Switzerland, Tetrahydrofuran (E.Merck). All chemicals and solvents were of an analytical reagent grade obtained from BDH.

Stock solutions of 0.1 M for each of KCl, NaCl, $CuSO_4$, $MnSO_4$, $ZnSO_4$, $AlCl_3.6H_2O$ and Folic acid were prepared by dissolving 0.3729, 0.2922, 0.7980, 0.7550, 0.806, 1.2075 and 2.207g in 50 mL of distilled water.

A stock standard solution of 0.01 M Fe(III) was prepared by dissolving 0.5031 g of standard solution and making the solution up to 50 mL with distilled water. The working solutions 10^{-7}-10^{-2} M Fe (III) were prepared by serial appropriate dilution of the stock solution. Stock solution of 0.1 M of HCl and 0.1 M of NaOH are used for adjusting pH of solutions

Procedure

Construction of ion-selective electrodes

The construction of the electrode body and the immobilization were done as described by Graggs et al[12] . The glass tube was 3/4 filled with 0.001 M Fe(III) solution as an internal filling solution. The membrane was conditioned by immersing in a standard solution of 0.01M Fe(III) for at least 2hours before measurements.

Preparation of Pharmaceutical Samples

The content of ten feroglobin capsules were mixed and weighted accurately. The weight average was equal to 0.4257 g per capsule is then dissolved and diluted to 1L with distilled water, the resultant concentration of Fe(III) is equal to 4.3×10^{-4} M. Other samples were prepared by dilution.

Selectivity measurements

A separate solution method[13] was used for the selectivity coefficient measurement, and was calculated according to the equation:

$$\log K^{pot}_{A,B}=(E_B-E_A)/S+(1-z_A/z_B)\log a_A \quad \ldots(1)$$

E_A, E_B; z_A, z_B; and a_A, are the potentials, charge numbers, and activities for the primary A ion, respectively, at $a_A = a_B$.

The selectivity coefficients were also measured by the mixed method [14] (Fixed interference method) according to the equation:

$$K^{pot}_{A,B}=a_A/(a_B)^{zA/zB} \quad \ldots (2)$$

Results and Discussion:

Four electrodes of Fe(III) (B1, B2, B3, B4) based on using the complex [CPSS-Fe(III)], with four plasticizers such as Di-butyl phosphate (DBP); Di-butyl phthalate (DBPH); Di-octyl phthalate (DOP); Tri-butyl phosphate (TBP); in PVC matrix were examined respectively. Non-Nernstian slopes were obtained for electrodes based on DBPH, DOP and TBP (membranes B2, B3 and B4).The slopes are, 24.60, 16.01 and 13.82 mV/decade with correlation coefficients of 0.9997, 0.9994 and 0.9998 respectively. The linear range for these electrodes $1x10^{-5}$-$1x10^{-2}$ M, $1x10^{-6}$-$1x10^{-2}$ M and $1x10^{-5}$-$1x10^{-2}$ M with detection limits of $7x10^{-5}$ M, $2x10^{-6}$ M and $9x10^{-5}$ M, respectively. The results and other parameters are given in Table (1). B1 electrode is the best electrode that gave the Nernstian slope of 19.79 mV/decade, with liner range $1x10^{-2}$–$1x10^{-5}$ M. This may be due to the compatibility between the components of the membrane, and the viscosity of DBP effect on the ion exchange between the membrane ions and the external solution ions. Consequently, DBP is more effective solvent mediator than other plasticizer due to its large dielectric constant. The long lifetime, good stability and reproducibility of electrode (B1) may be due to a high viscosity (≈112.88 CST), which prevents the leaching of complex to the external solution and causes a low mobility of ions in the matrix of the membrane. B2 electrode, gave a slope of 24.60 mV/decade, this high slope may be due the viscosity of DBPH which make steric of the ion exchange between the ion-pair [CPSS-Fe(III)] in membrane and the external solution. But the B4 electrode gave Non-Nernstian slope of 13.82mV/decade, this may be attributed to the low viscosity of TBP (3.11) and lead to leaching of the complex from the membrane to the external solution as well as decrease ion-exchange process between ion-pair of complex [CPSS-Fe(III)] in membrane and the external solution of, or may be attributed to the steric factor. A typical plot for calibration curves of electrodes based on four plasticizers DBP, DBPH, DOP and TBP are shown in fig.(2).

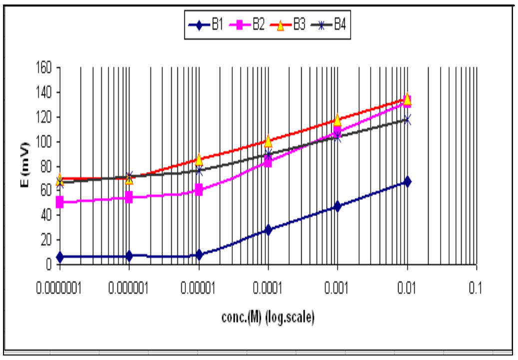


Fig. 2: Calibration curves of iron (III) selective electrodes using DPB, DBPH, DOP and TBP plasticizer

Table 1: The parameters for four Fe(III) electrodes

Electrode	Slope (mV/Decade)	Linear equation	Correlation coefficient (r)	Linear concentration range (M)	Detection limit (M)	Response time (sec)			Lifetime (day)
						10^{-2} (M)	10^{-3} (M)	10^{-4}(M)	
B1 CPSS-Fe(III)+DBP	19.79	y = 8.5947ln(x) + 107.29	0.9999	1×10^{-2}– 1×10^{-5}	9×10^{-6}	20	10	5	37
B2 CPSS-Fe(III)+DBPH	26.60	y = 10.6840 ln(x) + 182.60	0.9997	1×10^{-2}– 1×10^{-5}	7×10^{-5}	40	35	25	41
B3 CPSS-Fe(III) +DOP	16.01	y = 6.9531 ln(x) + 165.74	0.9994	1×10^{-2}– 1×10^{-6}	2×10^{-6}	25	15	10	23
B4 CPSS-Fe(III)+TBP	13.82	y = 6.0019 ln(x) + 145.27	0.9998	1×10^{-2}– 1×10^{-5}	9×10^{-5}	45	30	15	16

Effect of pH:-

The effect of pH on the electrode potentials for iron(III) selective membrane electrode (B1) was examined by measuring the e.m.f. of the cell in iron(III) solutions at two different concentrations (10^{-3}, 10^{-2}) M in which the pH ranged from (0.5-11). The pH adjusted by adding appropriate amounts of hydrochloric acid and/or sodium hydroxide solution. The results shown in fig.(3). At pH values less than 1.5 or in very high acidity, the hydrogen ions diffuse through the membrane until equilibrium between the external and internal. But at pH higher than 6, some iron (III) hydroxide was form in the solution, this causes deviation in the electrode response. The working pH ranges were tabulated in Table2

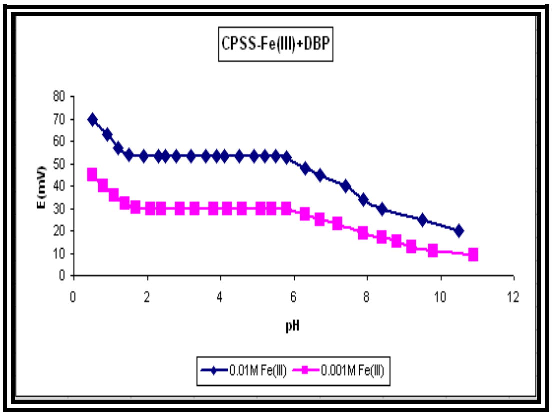


Fig. 3: Effect of pH on the potential of the electrode B1 at concentrations 10^{-2} and 10^{-3} M

Table 2: Working pH ranges for Fe(III) electrode (B1).

Electrode no.	Composition of electrode B1	PH range	
		10^{-2}M	10^{-3}M
B1	**(CPSS-Fe(III) +DBP)**	**1.5-6.0**	**2.0-6.0**

Selectivity methods

In order to investigate the selectivity of the proposed membrane (B1) ion selective electrode toward Fe(III) with respect to various interfering ions, a separate solution method was used. The calculated values of the selectivity coefficients using equation 1 are listed in Table 3.

In mixed method, The potential values obtained are plotted vs. the logarithm of the concentration of the Fe(III). The intersection of the extrapolated linear portions of this plot indicates the value of (a_A) as show in fig. (4). The calculated selectivity coefficients in Table 3, indicate that there is no significant influence on potentiometric response of the proposed PVC-membrane electrode toward Fe(III) which caused by interfering of different species used for test.

Table 3: Values of $K^{pot}_{A,B}$ according to separate and mixed methods by using electrode B1

Interfering ions	Separate method	FIM	
		$a_B=5\times10^{-2}$	
		a_{CPSS}	$K^{pot}_{A,B}$
k^+	3.35×10^{-3}	9.0×10^{-6}	7.2×10^{-2}
Na^+	1.04×10^{-3}	8.0×10^{-6}	6.4×10^{-2}
Cu^{+2}	2.09×10^{-3}	1.8×10^{-5}	1.6×10^{-3}
Mn^{+2}	1.19×10^{-2}	3.5×10^{-5}	3.1×10-3
Zn^{2+}	3.74×10^{-3}	2.5×10^{-5}	2.2×10^{-3}
Al^{3+}	4.08×10^{-1}	1.4×10^{-4}	2.8×10^{-3}
Folic acid	1.87×10^{-3}	7.0×10^{-6}	5.6×10^{-2}

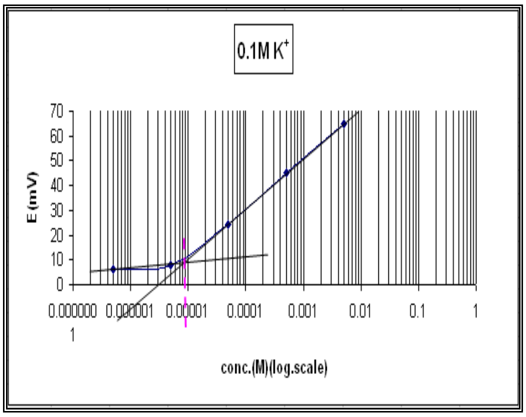


Fig. 4: calibration curve of mixed method Fe(III) selective electrode (B1).

Sample analyses:-

Four potentiometric techniques were used for the determination of Fe(III) including, Direct method, Standard addition method (SAM) follows the equation:

$$C_U = C_S / 10^{\Delta E/S} [1+ (V_U / V_S)] - (V_U / V_S)$$

Where C_U, C_S, V_U and V_S are the concentration and volume of unknown and standard solution respectively.

In the multi standard addition method (MSA), the plot of anti logarithm (E/S) versus the volume of the multiple addition of the standard solution was used to determine the concentration of Fe(III). A typical plot is shown in fig.(5) . The results are listed in Table 4.

For potentiometric titration a 10^{-1} M of sodium hydroxide was used as a titrant. A typical titration plot is shown in fig.(6). The recovery (Re %), relative error (E_r %) and relative standard deviation (RSD %) for each method are calculated and listed in Table 4.

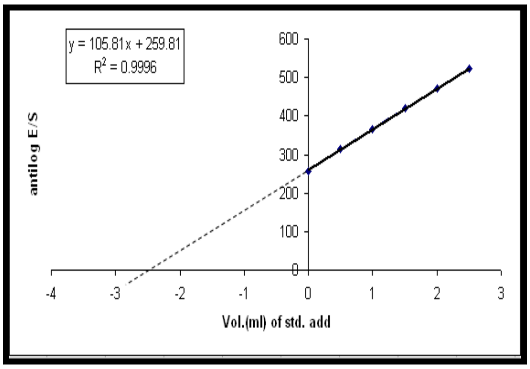
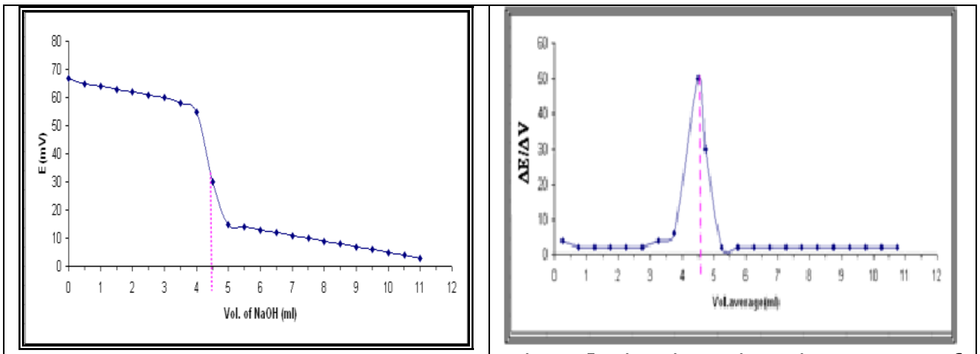


Fig. 5: Plot of antilog (E/S) versus the volume of iron(III) using B1 electrode.



Titration curve of electrode (B1).

First *derivative* Titration curve of electrode (B1).

Fig.(6) Titration curves of iron(III) selective electrode using DBP plasticizer.

The electrode (B1) was proved to be useful in the potentiometric determination of Fe(III) in pharmaceutical preparations and the data obtained for pharmaceutical samples are listed in Table 5. The ion selective electrode method, however, appears to be more attractive in terms of sensitivity selectivity and simplicity and wide range.

Table 4: Analysis of iron(III) by potentiometric techniques

Parameter	**Direct method**	**SAM**	**MSA**	**Titration Method**
Conc.(M)	1.000×10^{-4}	1.000×10^{-3}	1.000×10^{-3}	1.000×10^{-2}
Found(M)	1.004×10^{-4}	0.9992×10^{-3}	0.982×10^{-3}	1.001×10^{-2}
RSD*%	0.501%	0.426%	-----------	0.141%
Re%	100.4%	99.9%	98.2%	100.1 %
relative error%	0.4%	-0.1%	-1.8%	0.1 %

Table 5: Sample analyses of Feroglobin capsules pharmaceutical

Parameter	**Direct method**	**SAM**	**MSA**	**Titration Method**
Conc.(M)	1.000×10^{-3}	1.000×10^{-3}	1.000×10^{-3}	1.000×10^{-3}
Weight(g)	0.0558	0.0558	0.0558	0.0558
Found(M)	0.999×10^{-3}	0.997×10^{-3}	0.996×10^{-3}	1.001×10^{-3}
mg/ capsule	23.975	23.979	23.961	23.970
RSD*%	0.978%	0.828%	-----------	0.141 %
Re%	99.9%	99.7%	99.6%	100.1 %
E_r%	-0.1%	-0.3%	-0.4%	0.1 %
S	9.782×10^{-6}	8.264×10^{-6}	-----------	----------
$x \pm (ts/\sqrt{N})$	$0.999\times10^{-3}\pm0.122\times10^{-4}$	$0.997\times10^{-3}\pm0.102\times10^{-4}$	----------	-----------

RSD*% for n=5, t=2.78

Conclusions:

ISE method included fabrication of membranes for Fe (III) was constructed based on using the complex [CPSS-Fe(III)] and many plasticizers. The best electrode for Fe(III) was (B1) using DBP as plasticizer . B1 is the electrode which used to determine Fe(III) in the pharmaceutical sample. Also there is no interference for some interfering ions. The proposed analytical method is proved to be simple and rapid, with good accuracy.

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تصنيع اقطاب انتقائية جديدة لتقدير الحديد الثلاثي وتطبيقاتها في المستحضرات الصيدلانية

خالدة حميد السعيدي* ***وئام رعد عزيز****

*قسم الكيمياء/ كلية العلوم/ جامعة النهرين.

الخلاصة:

حضرت أقطاب انتقائية سائلة لتقدير الحديد الثلاثي والتي تعتمد على المعقد (الكلورامفينيكول صوديوم ساكسينيت مع الحديد الثلاثي) مع أربعة من الملدنات، داي بيوتيل فثاليت، داي بيوتيل فوسفيت، داي اوكتيل فثاليت وتراي بيوتيل فوسفيت مع بوليمر الفاينيل كلورايد. اعطت هذة الأقطاب انحدارا نيرنيستي و شبه نيرنيستي 19.79، 26.60، 16.01 و 13.82 ملي فولت/حقبة ومدى التركيز الخطى حوالي من 10^{-5} الى 10^{-2} على التوالي. وكان أفضل قطب الذي يعتمد على داي بيوتيل فوسفيت كملدن حيث اعطى انحدارا 19.79 ،معامل ارتباط 0.9999 ، حد كشف $9X10^{-6}$ وعمره 37 يوم مع استفرارية وتكرارية جيدة , لتقديرالـ حدي د الثلاثي في المستحضرات الصيدلاتية.كذلك درست التدخلات لحساب معامل الانتقائية بطريقة المحاليل المنقصلة وطريقة المحاليل الممزوجة بوجود الايونات المواد التالية(K^+, Na^+, , Al^{+3}, Cu^{+2}, Mn^{+2},Zn^{+2},Folic acid) ودراسة حدود الدالة الحامضية وعمر القطب.