Preparation and study of Chloride – Liquid Selective Electrode based on quaternary ammonium salts in PVC matrix

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Abstract

Chloride selective electrodes based on PVC matrix membrane consist of various alkyl quaternary ammonium salts such as tetra heptylammonium chloride (THACl), and tetraoctylammonium. chloride (TOACl) as a sensors with various mediators were prepared and studied.

The study includes the electrodes parameters determination (slope, linear response range, detection limit , pH effect , life time and selectivity). Chloride electrode based on (TOACl) as sensor with di-n-octyl phthalate (DOPH) as mediator gives excellent response with a slop equal 60.1 mV/decade which is the near to the Nernstian slope. Concentration was ranged from 10-2 M to 10-4 M with detection limit around 10-5 M. This electrode was used for chloride determination ion in samples using different potentiometric methods.

Introduction

The determination of chloride in natural water is important because it is contained in domestic effluents of industrial sewage and its concentration can be regarded as indicator of water pollution.

Potentiometric titration with silver nitrate is a precise method for the determination of chloride (1). But because direct potentiometer using chloride ion – selective electrode is both rapid and simple, it is a more suitable technique for the analysis of waters. Many papers have been published on the direct potentiometeric determination of chloride in natural water (2), due to interference of bromide, sulfide and other ions. Therefore, pretreatment is usually required for water analysis (3,4).

Liquid membrane based on tetraalkylammonium chloride have been used for chloride determination in clinical chemistry such as blood, urine and sweat samples (5).

Aliquat 336S also known methyltrioctylammonium chloride has been widely used as an anion component in liquid membrane electrode systems (6).

Toullec et al.(7) used chloride ion selective electrode for the monitoring reactions, of relatively fast kinetic processes. t1/2 approximate to 40 seconds and applied to the hydrolysis of yperite analogues in presence of oximate nucleophiles.

Sjoberg et al.(8) prepared solide state chloride selctive electrodes with plasticizer-free membrane by incorporating tridodecylmethyl ammonim chloride(TDMACl) in a semi conducting conjugated polymer matrix of poly-octylthiophene (POT).The interferce from lipophilic anions ClO4- ,ScN- ,NO3- and Br- was significantly reduced in comparison with chloride electrodes based on TDMACl and plasticized PVC.

Rakhman(9) developed a chloride-sclective electrodes based trinonyloctadecylammonium trichloromercurate. This electrode exihibts much higher selectiviyy for NO3 and hydrocarbons ions than ion- selective electrode based on quaternary ammonium chloride.

In this work, tetraheptylammonium chloride and tetra octyl ammonium chloride have been used as sensors with various solvent mediators to prepare several electrodes for the measurement of chloride ion.

Experimental

Equipment:

1. Expendable ion analyzer ,type Orion model EA 940,measured the electrode potential.
2. pH meter type Orion EA 940 was used for pH measurement.
3. Reference electrode, types saturated calomel electrode (SCE).

Reagents:

1. Quaternary ammonium salts such as tetraheptylammonium chloride (THACl) and tetraoctylammonium chloride (TOACl) were obtained from Fluka Chemie.A.G.
2. Plasticizer are di-n-octyl phthalate (DOPH),o-nitro phenyl octyl ether (NPOE) and tri –n-butyl phosphate (TBP) were obtained from BDH.and Fluka Chemie. A.G.
3. Poly vinyl chloride (PVC) high molecular weight polymer type breon 113,b.p chemicals(U.K) Ltd.
4. Other salts and solvent to be used are analytical reagent grade .
5. All solutions were prepared using deionized water.

Procedure:

Membrane and electrode construction:

The membrane was prepared as described in reference (10). The membranes were prepared by dissolving 0.04g sensor +0.36g plasticizer +0.17g PVC in 6ml tetrahydrofurane (THF), this solution

was poured into a glass ring (30-35 mm. diameter),place a pad of filter paper with a heavy weight on a top of the glass ring, followed by slow evaporation of the solvent at least takes two days.

The electrode was constructed as described in reference (10) which consist of glass tube with internal silver wire coated with silver chloride in 0.1M sodium chloride filling solution.
The membrane was fixed at the end of the electrode.

Calibration curve:

Calibration curves were obtained by calibrating the electrode in various concentrations of sodium chloride (10-1M-10-6M). A calibration graph was plotted between log concentrations and electrode potentials.

Selectivity of the electrode:

The interference of various common anions such as nitrate, bromide sulfate and acetate was studied by the mixed solution method (11,12).

Effect of pH:

The effect of the pH of the test solution (10-3M) NaCl, on the electrode potential was investigated following the variation in potential with change in pH produced by addition of small volume of sodium hydroxide or hydrochloric acid.

Results and discussion

The response characteristics of the electrodes based on the term alkylammonium chloride (THACl, TOACl) as sensors with different solvent mediators are summarized in Table (1). The electrodes were conditioned by soaking in aqueous 10-1M sodium chloride for 24 hours before the calibration.

The electrodes based on THACl membrane Nos. (I, II, III,) give a slope ranged from 55.1 to 60.7 mv/decade, which is similar to the Nernstain slope (59.1mv/decade) with a detection limit around 10-4M and concentration range from 5x10-1 M to 10-4 M.

The membranes (IV, V, VI,) based on (TOACl) gives better results for the electrodes parameters than (THACl) , in which the detection limit reached about 10-5 M and concentration ranged from 10-4 M to 10-2 M with (r) ranged from 0.9980 to 0.99993.These membranes are suitable for low concentration determination of chloride.

Fig(1) shows typical calibration curves for the electrodes based on (TOACl) and (THACl) as sensors with (DOPH) as solvent mediator.

The effect of pH on the electrodes based on (TOACl) as sensor with different mediators was investigated and the results of pH range are listed in table (2).

Fig.(2) shows the effect of pH on the response of electrode based on (TOACl) as sensor.

The figure shows that the potential are fixed from pH 4.5 to 8.5, otherwise deviation in potential were noticed at pH< 4.5, pH > 8.5, this was attributed to the hydrogen and hydroxide ions interference.

The life time was also investigated for all electrodes. The electrodes based on membranes Nos.(II, VI,) could be used at least 3 weeks, which for membrane Nos. (III, IV,) for around 7 weeks.

Selectivity coefficient was also determined for the interfering anions, nitrate, acetate, bromide, and sulfate .It is difficult to measure the selectivity for chloride in the presence of these anions because instable of the electrode response. That is means the interfere of these ions on electrode response for chloride.

The electrode based on (TOACl) as sensor and (DOPH) as mediator that gives better results for electrode parameter was used to check the chloride concentration in synthetic solution of chloride.

The results of potentiometric determination using (D.M, G.P, S.A, and M.S.A) are listed in Table (3).

The relative error (R.E) for (D.M) was calculated and it is about 4% while a high value of (R.E) 7% in using (M.S.A) As we noticed that the relative error was increased as the concentrations of chloride ion decrease.

Table (1): Specific parameters for the electrodes based on membrane consist of quaternary ammonium chloride with different solvent mediators

Membrane no.	Solvent mediator	Slope mV/decade	Concentration Range/M	Detection limit	Correlation coefficient
I	NPOE	55.2	10-1 - 10-3	4x10-4	0.9990
II	DOPH	57.5	10-1 –10-3	2x10-4	0.9990
III	TBP	60.1	10-1 - 5x10-4	10-4	0.9998
IV	DOPH	61.2	10-2 - 10-4	10-5	0.99993
V	NPOE	56.2	10-2 - 10-4	5x10-5	0.9980
VI	TBP	57.6	10-2 –10-4	10-5	0.9980

Membranes No. (I,II,III) depend on (THACL) as sensors.
Membranes No. (IV,V,VI) depend on (TOACL) as sensors.

Table (2): Working pH – ranges for electrodes based on (TOACl) as sensor.

Membrane No.	pH-range
DOPH	4.5 - 8.5
NPOE	6 - 10.5
TBP	6.5 - 10.5

Table (3): Recovery of chloride ion using electrode based membrane No.(IV)

Concentration of chloride ion	Direct method D.M	Gran plot (G.P)	Standard addition S.A	Multi standard addition M.S.A
10-3	9.9x10-4	1.05x10-3	9.93x10-4	9.93x10-4
RE	4%	5%	7%	7%
10-4	9.96x10-5	9.93x10-5	9.94x10-5	1.1x10-4
RE	4%	7%	6%	10%

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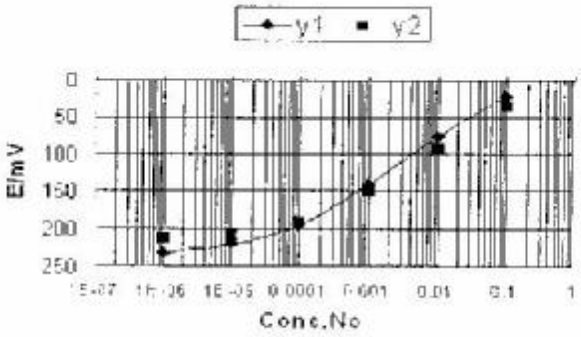

Figure (1): Calibration curve for the electrodes based on TOACl (y1) and THACl (y2) as sensors with DOPH as solvent mediator

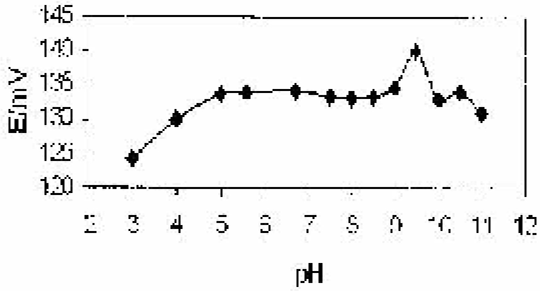

Figure (2): Effect of pH on the response of chloride selective electrode based on TOACl as sensor with DOPH as solvent mediator.

الخلاصة

تم تحضير ودراسة أقطاب الكلوريد المتمثلة في مادة الـ PVC والمتكونة من أغشية محتوية على أملاح الأمونيوم الرباعية التي تعمل كمواد فعالة لأيون الكلوريد وهي كلوريد رباعي هكسيل الأمونيوم (THA-Cl) ورباعي اوكتيل كلوريد الامونيوم (TOA-Cl) مع مواد مذيبة مختلفة.

من خلال الدراسة تم تعيين مواصفات هذه الأقطاب والتي تتضمن انحدار نرنست، مدى التركيز، مدى التحسس، تأثير الـ pH، عمر القطب وكذلك الانتقائية.

لوحظ ان القطب المتكون من (TOA-Cl) كمادة فعالة مع المادة المذيبة داي اوكتيل فثاليت (DOPH) يعطي استجابة ممتازة مع انحدار مساوي الى 61.1 mv/decade وهو مقارب الى انحدار نرنست مع مدى تركيز يتراوح من 10-4.1 M الى 10-2M ومدى تحسس مساوي الى 10-5M. واستخدم هذا القطب في تعيين الكلوريد في نماذج مختلفة باستخدام الطرق الجهدية المباشرة.