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RESEARCH ARTICLE

PREPARATION OF CHLORIDE SELECTIVE MEMBRANE ELECTRODE

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ABSTRACT

In this study, the novel membrane chloride-selective electrode consisting of 30% of tridodesylmethylammoniumchloride (TDMC) as the active material, 50% of PVC as the membrane matrix and 20% of dibutylphatalate (DBF) as the plasticizer wasdeveloped. In this electrode, the potential change occurs from 10^{-5} to 10^{-1} M chloride ion and the slope of linear portion corresponds to 55,0± 2,0mV per decade change of chloride concentration. Furthermore, the interference effects of some ions, such as F^-, I^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Cu^{2+} and Fe^{3+} were not observed.The response time and lifetime of electrode was 60 s and 6 months, respectively. It has been observed that pH did not affect the sensitivity of the electrode. This electrode has been used for the direct determination of 32,0 ± 0,5 mg/L chloride in the spring water.

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INTRODUCTION

In the literature, there were several liquid and polymer membrane-based ion-selective electrodes (ISEs) used for the determination of chloride [Oka, 1981; Hartman, 1978; Willis, 1983; Hitachi, 1982; Coetzee, 1968; Coetzee, 1969].The active components in these electrodes werethe quaternary ammonium salts. The innate Hofmeister-type response of such sensors to lipophilic anions, such as salicylate, can lead to significant positive errors for determination of chloride in the blood samples obtained from patients with ingestedAspirin [Lewandowski, 1989]. Additionally, the positive interferences of bromide and added heparin can be also observed [Park, 1991]. The researchers developed a method for the fast preparation of chloride selective electrodes (Ag/AgCl electrodes) by dipping silver wire into the sodium hypochlorite solution [Jiang, 2015]. They were prepared bydifferent immersion time. Someproperties of them, such as Nernst response, response time and long-term stability, were tested in the simulated concrete pore solutions (SCPS) [Duffó, 2009; Climent, 1996]. In principle, the determination of chloride is important in many different fields,such as clinical diagnosis [Jiang, 198; Huber, 1998] environmental monitoring [Huber, 2000; Martin, 1997] and various industrial applications [Badr, 1999; Ratjen, 2003].

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In general, the chloride ions associated with ions Na^+, K^+; $Mg^{2+}$are present in the sea water and sediments of the Earth's crust in large quantities.Moreover, they are widely distributed tothe nature as salts, such as NaCl, KCl, and $CaCl_2$ [Department of National Health and Welfare, 1978].We have developed a new chloride selective electrode because of the fact that the determination of chloride in the spring water samples is essential [Somer, 2001]. The aim of this work was to prepare aselective electrode for chlorideusing ion exchanger as the active material. For this, the solid membrane electrodes were prepared using tridodesylmethyammoniumchloride (TDMACl), PVC anddibutylphtalate (DBF) in different compositions which were used as ion exchanger active material, inert matrix and plasticizer, respectively. Furthermore, their optimum working conditions were also investigated in detail and the interference studies were also performed.Then, the chloride ion in the spring water was determined by this prepared electrode.

Experimental

Apparatus and reagents: The potential was measured with JENWAY 3030 Ion Analyser. While a double junction Ag/AgCl electrode, 924036, was used as the outer reference electrode, as the inner reference electrode, the home-made Ag/AgCl electrode was prepared; it was immersed into a 0.1 M NaCl and 0.1 M KI solution. For the pH measurements, the ion analyser with 924003 combined with pH electrode was used. All measurements were performed with a 30 mL glass cell prepared for this purpose. A magnetic stirrer was used throughout the experiments.

All reagents (NaCl, KBr, NaF, KI, $Fe_2(SO_4)_3$, $CuCl_2$, $AgNO_3$) were of at least analytical reagent grade (Merck). Triply distilled water purification system was used for the preparation of all solutions.

Preparation of electrode: 100–250 mg of PVC dissolved in 3 mL tetrahydrofuran (THF), 90 mg of ion exchanger dissolved in 1 mL THF and 0.2 mL of DBF were mixed in a 30 mL beaker with a diameter of 4.2 cmand then the mixture was stirredby a magnetic stirrer. The solvent was then allowed to evaporate at ambient atmosphere for about 24 h. The membrane formed as a film in the bottom of the beaker was taken out carefully using Teflon forceps. Then, the film membrane was cemented to the flat end of a PVC tube (1 cm diameter) with an adhesive of PVC dissolved in THF. One day later, the excess membrane was cut and the tube was filled with 0.1 M NaCland 0.1 M KI solution, respectively. A home-made Ag/AgCl electrode was then immersed as the inner reference electrode. For conditioning of theelectrode, it should stay in 10^{-4} M NaCl solution for about 2days [19].

RESULT AND DISCUSSION

Calibration curves of the electrode: The potentiometric responses of the prepared electrodes were investigated against chloride concentration. For this purpose, appropriate amounts of chloride ions were spiked to the cell and the corresponding potentials were recorded. For a fixed ionic strength, all measurements were made in 0.1 M $NaNO_3$solution.The potential readings were plotted against pCl.The slope of the electrode was found as about 58 mV and it was not changed for more than 6 months.

Effect of membrane composition and thickness: It is known that the detection limit, selectivity and the maintenance of the electrode depend on membrane composition and thickness. For this reason, the electrodes in different membrane compositions and thickness were prepared and their potential responses were measured inthe range from 10^{-6} to 10^{-1} M chloride concentration for each 10times of concentration change.By the time membrane mixtures in different weight quantities were used in the same size of beakers, the thickness of membranes was also different. The membranes in 30% of TDMACl, 50% of PVC and 20% of DBF composition but at different masses (0.2, 0.3, 0.4 and 0.5g) were prepared and they were used as the active materials. For each electrode, the potential responses were measured at different chloride concentrations. In the concentration range from 10^{-5} to 10^{-1} M chloride, the slopes for 0.2, 0.3, 0.4 and 0.5 g of electrodes were about 24, 21, 58 and 31 mV, respectively (Fig. 1). It is known that the membrane thickness also plays an important role for the response of the electrodes. While the response time was short with thin membranes, its mechanical strength became less. Finally, it was found that the electrode with a total mass of 0.4 g had both the highest slope and good mechanical strength. Furthermore, to investigate the effect of composition, the electrodes in 0.4 g weight were prepared in different active material ratios, changing from 10 to 30% of TDMACl. The measured slopes of electrodes in different compositions were summarized in Table 1.As seen, because the electrode with 30% of TDMACl had the highest slope (about 58 mV), this electrode was used throughout the whole study.

The response time of electrode: The response time of the electrode was measured for different chlorideconcentrations because it depends strongly on the concentration change.

Table 1. Effect of membrane composition on the response time of electrode (0.4 g) in 0.1 M $NaNO_3$

$[F^-]$ (M)	E (mV)		
	10%TDMACl, 60%PVC, 20%DBF	20%TDMACl, 60%PVC, 20%DBF	30%TDMACl, 50%PVC, 20%DBF
$1x10^{-5}$	192	180	152
$1x10^{-4}$	174	155	100
$1x10^{-3}$	150	125	40
$1x10^{-2}$	131	90	-20
$1x10^{-1}$	105	50	-80
$1x10^{-5}$ to $1x10^{-1}$ M Slope	21.8	32.5	58.0

Table 2. Selectivity coefficients $(K_{A,B}^{pot})$for the chloride selective electrode in mixed solutions (in the presence of $1x10^{-5}$ M Cl^-)

Ions	$K_{A,B}^{pot}$
Cl^-	$2x10^{-3}$
NO_3^-	$6x10^{-4}$
SO_4^{-2}	$7x10^{-6}$
PO_4^{-3}	$3x10^{-4}$
K^+	$2x10^{-3}$
Na^+	$1x10^{-3}$
Ag^+	$1x10^{-5}$
Ca^{+2}	$2x10^{-6}$
Cu^{+2}	$3x10^{-6}$
Mg^{+2}	$3x10^{-6}$

Table 3. Chloride analysis in tea and comparison of results with commercial electrodes

Ion	Developed electrode	Commercial (Orion) electrode	$t_{experimental}$ $t_{critical}$=2,53
$[Cl^-]$ (mg/L)	32 ± 0.5	33 ± 0.6	0,42

95% CI and N=5

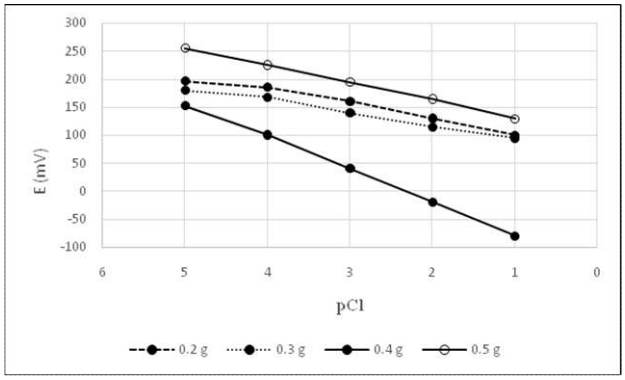

Fig. 1. Effect of membrane thickness on calibration curves (30% TDMACl, 50% PVC and 20 % DBF).

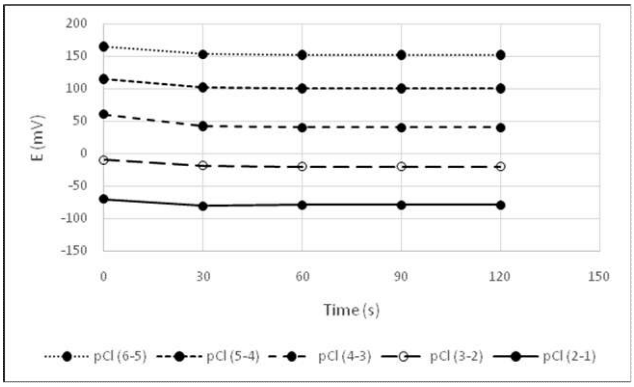

Fig. 2. The dependence of response time on the change of concentrations

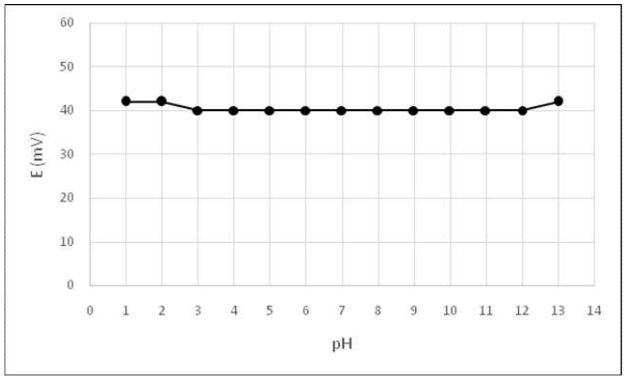

Fig. 3. Variation of the chloride electrode potential at 1.0x10-3 M concentration with pH

For this purpose, the potential values based on time were recorded at different chloride concentrations. The response time of the electrode was found as 1 minute (Fig. 2).

Effect of Ph: The pH effect on the potential readings at 10^{-3} M chloride concentration was investigated in detail. For this purpose,the 10^{-3} M chloride solutionwas prepared and the pH of this solution was adjusted to certain values by the addition of both HCl and NaOH using a pH meter. For chloride concentration, the measured potentials at each pH values were plotted againstpH. The potential readings remained unchanged within the pH range of 2–12 at 10^{-3}M chlorideconcentrations of chloride (Fig. 3).

Interference studies: The possible interference effects of some anions (F^-, Br^-, I^-, SO_4^{2-}) and cations (Na^+, K^+, Cu^{2+}, Fe^{3+}) were investigated. For this, selectivity coefficients mixed solution method was preferred as it usually corresponds more closely to the situation in the samples.In this method, solutions were prepared with a constant activity ofthe main ion (chloride) while varying activity of interfering ion. For this purpose, the interfering ion was added to 10^{-3} M chloride solution (in 0.1 M $NaNO_3$) so that its concentration was 10^{-2} to 10^{-3} M and after each addition, the change of potential was measured. Based on the experimental results, no interference effect was observed for F^-, Br^-, I^-, SO_4^{2-} and for Cu^{2+}, Fe^{3+}.

The selectivity coefficients for the interfering ions were also calculated by using the mixed solution method [20].

$$K_{A,B}^{pot} x a_B^{nA/nB} = a_A\{\text{antilog}[(E_1 - E_2)/S]\} - a_A \quad (1)$$

where $S = 2.303RT/n_A$ (the slope of chloride electrode), a_A is the activity of the primary ion, $a_B$is the activity of the interfering ion, $E_1$is the potential measured when only A is present, $E_2$is the potential responsive to the primary ion in the presence of interfering ioni$K_{A,B}^{pot}$the selectivity coefficient and n_A, n_B are the charges of A and B, respectively. For the determination of the selectivity constant, the$a_B^{nA/nB}$values were plotted against the right hand side of E_q. (1) and the slope was equal to the selectivity coefficient of the interfering ions. The selectivity coefficients obtained for some anions and cations were given in Table 2.

Determination of chloride in spring water: For this purpose, 500 mL of spring water sample was taken for the determination of chloride ion.The potential measurements in the sample including 0.1 M $NaNO_3$were made using both the commercial electrode and the electrode prepared in this study.For the determination of chloride ion in the sample, different calibration graphs were drawn for both electrodes. From both calibration graphs, while the chloride concentration was determined as 33.0 ± 0.6 mg/L with commercial (Orion) electrode,it was determined as 32.0 ± 0.5 mg/L with the newly prepared electrode. The results were given for both electrodes based on 95% of confidence level using five different samples. The t-test was performed to compare the means of the results obtained from both electrodes. Based on the calculations, the results of both commercial and electrode prepared in this study were similar shown inTable 3.

Conclusion

In this proposed study, the new a selective electrode was used for the determination of chloride. This electrode showed 58 mV sensitivity to chlorideconcentrations in the range from 10^{-5} to 10^{-1} M. As a result of the analysis,the chloride concentration in the springwater sample was found to be 32 ± 0.5mg/L based on 95% of confidence level in five measurements.

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