Polymeric Iodide-ion Selective Electrodes Based on Urea Derivative as an Ionophore

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The polymeric membrane electrodes based on urea derivative as an ionophore were prepared and studied for the iodide-ion selective electrode. This membrane exhibits a linear stable response over a wide concentration range (1.0×10^{-5}–1.0×10^{-2}) with a slope of −57.7 mV/decade, a detection limit of $\log[I^-] = -5.63$, and a selectivity coefficient for iodide against perchlorate anion ($\log K_{I^-}^{pot} = -1.42$). The selectivity series of the membrane gives the follow as $I^- > SCN^-$, $Sal^- > ClO_4^- > NO_3^- > Br^- > NO_2^- > Cl^- > F^-$. The proposed electrode showed good selectivity and response for iodide anion over a wide variety of other anions in pH 5.0 buffer solutions.

Key Words : Polymeric membrane electrode. Urea derivative, Ionophore, Iodide-selective electrode

Introduction

Many cations can be selectively and sensitively determined by direct measurement with ion-selective electrodes (ISEs), but the selective determination of many anions has a crucial drawback such as the classical Hofmeister series which is correlated with use anions. Therefore, the need for ionophores with improved selectivities and sensitivities in the field of anion-selective electrodes is increased.

A study on anti-Hofmeister sensing materials with high selectivity for given anions is an expeditiously expending domain in the field of chemical sensors. Membranes based on ion exchangers, such as lipophilic quaternary ammonium or phosphonium salts, display the classical Hofmeister behavior,[1] in which the membrane selectivity is controlled by the free energy of hydration of ions involved with a selectivity sequence: $ClO_4 > SCN > I \approx Sal > NO_3 > NO_2 > Br > Cl \approx HSO_3 > CH_3COO \approx HCO_3 > HSO_4 > SO_4^{2} \approx H_2PO_4 \approx F$.[2,3] Recently, electrodes using plasticized poly(vinyl chloride) (PVC) membranes incorporating lipophilic organometallic compounds,[4,5] metalloporphyrins,[6-9] metallophthalocyanines[10-12] and Schiff-base metallic complexes[13-19] have been reported, which have demonstrated potentiometric anion selectivity sequences that deviate from the Hofmeister pattern. These deviations result from a direct interaction between the central metal of the membrane-active components and the analytical anion and steric effect associated with the structure of the ligand. Because iodine is an indispensable microelement to humans, the determination of iodide ion is very important, especially in environmental, medicinal and food samples. Several iodine ion-selective electrodes based on a variety of ion carriers have also been reported in the literature.[13,14,20-22] In the previous study, compounds having urea derivative have presented good selectivity for fluoride anion by spectroscopic and NMR study.[23] Therefore, in the present work, thio-urea derivative (see Figure 1) were synthesized in our laboratory to prepare highly selective iodide electrodes. An electrode containing this ionophore with 2-nitrophenyloctylether (*o*-NPOE) as a plasticizer demonstrated a highly selective and sensitive response to iodide with a substantially improved performance, such as wide potentiometric response range, low detection limit and interference from other anionic species.

Experimental

Reagents. Urea derivative (Figure 1: [2-(3-(4-nitrophenyl)thioureido)-*N*-(4-nitrophenylcarbamothioyl)benzamide]) tested as iodide ionophore was prepared according to the procedure described previously.[24] High molecular weight PVC, dioctyl sebacate (DOS), dioctyl adipate (DOA), dioctyl phthalate (DOP), 2-nitrophenyl octyl ether (*o*-NPOE), tridodecylmethylammonium chloride (TDDMACl) and tetrahydrofuran (THF), which were obtained from Fluka, were used to prepare the PVC membranes. Analytical grade sodium salts of tested anions were used. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions.

Preparation of polymeric ion-selective electrodes. The compositions of PVC-based iodide-selective electrodes were

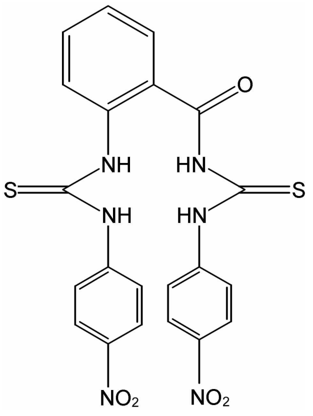

Figure 1. The structure of urea derivative used as an ionophore.

Table 1. The compositions of membrane and their potentiometric characteristics of the iodide-selective electrodes in pH 5.0 buffer solutions

Membrane	Ionophore[a]	PVC[a]	*o*-NPOE[a]	DOS[a]	DOP[a]	DOA[a]	DBS[a]	TDDMACl[b]	LOD (loga)	Slope (mV)
m-1	1	33	66					0	−5.61	−34.5
m-2	1	33	66					50	−5.63	−57.7
m-3	1	33		66				50	−4.37	−45.0
m-4	1	33			66			50	−4.46	−50.0
m-5	1	33				66		50	−4.93	−46.8
m-6	1	33					66	50	−3.59	−45.9
m-7	2	33	66					50	−5.18	−51.3
m-8	3	33	66					50	−5.13	−52.9
m-9	5	33	66					50	−5.06	−52.3

[a] In milligrams. [b] Mole percent relative to the ionophore.

summarized in Table 1, and the typical one was 33 mg PVC, 66 mg plasticizer, 1 mg ionophore and TDDMACl (50 mol% of ionophore). The ionophore, plasticizer and PVC were dissolved in the appropriate volume of THF and mechanically stirred. All membrane cocktails were cast in glass rings placed on glass plates for conventional ion-selective electrodes. Solvent from PVC membrane was allowed to evaporate for at least 24 hours at room temperature. The thickness of the resulting membrane measured by micrometer was about 0.3 mm.

Potentiometric measurements. The electrochemical properties of iodide-selective electrodes were investigated in the conventional configuration. Small disks were punched from the cast membranes and mounted in Philips electrode bodies (IS-561). For all electrodes, 0.1 M KCl solution was used as an internal filling solution. All electrodes were finally conditioned for 24 h by soaking in 1.0×10^{-2} M NaI solution. A silver/silver chloride coated wire was used as an internal reference electrode. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference electrode (Model 90-20) with two chambers. This reference electrode has two different filling solution : inner chamber filling solution is green colored solution saturated with AgCl, outer chamber filling solution consists of 10% KNO_3. The potential measurements were carried out at 25 ± 1 °C with Kosentech 16-channel potentiomerter (KST101-1) coupled to a computer by setting up the following cell assembly: Ag/AgCl/0.1 M KCl/PVC membrane/test solution/Ag/AgCl. The electrochemical measurements were conducted after within 1 mV variance of open circuit potential with 5 minutes. The dynamic response curves were produced by adding standard solutions of anions to magnetically stirred buffer solution (0.05 M Tris-HCl). The selectivity coefficients (log $K_{I,j}^{pot}$) were determined by the separate solution method (SSM) using sodium salts of the anions involved. Detection limits were estimated at the intersection of two linear lines, the one extrapolated from a high concentration range and the other parallel to the X-axis drawn through the mean potential value of the lowest anion concentration used in the plot of the potential change and the concentration of I^-.

Results and Discussion

Supramolecules as an anion ionophore should bind selectively specific anion, and have kinetically fast exchange and sufficient lipophilicity. The pH dependence of potentiometric response was investigated in different pH (0.8 to 7.0) buffer solutions. The effect of pH on the potentiometric response of the novel electrode prepared with urea derivative as an ionophore (66 mg *o*-NPOE, 33 mg PVC, 50 mol% TDDMACl, and 1 mg urea derivative) is studied in 0.05 M Tris-HCl buffer solutions at different pH values, and shown in Figure 2. The results indicate that the potentiometric response toward iodide ion depends on the buffering pH values. According to experimental results, when the solution pH was increased from 0.8 to 7, the slope and detection limit of the membrane was slightly changed. The best slope and detection limit were obtained at pH 5.0: the slope of −57.7 mV/decade and the detection limit of $\log[I^-] = -5.63$. This sub-Nernstian is for a monovalent anion response. When considering the small difference of initial potential at different pHs in Figure 2, the hydroxide anion activity slightly affects to the potentiometric response of the membrane. It

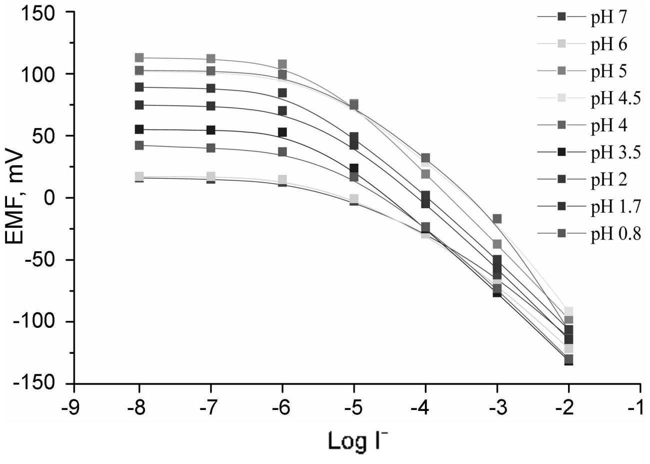

Figure 2. Potentiometric responses of the iodide ion-selective electrodes based on the ionophere (m-2) in various pH buffer solutions.

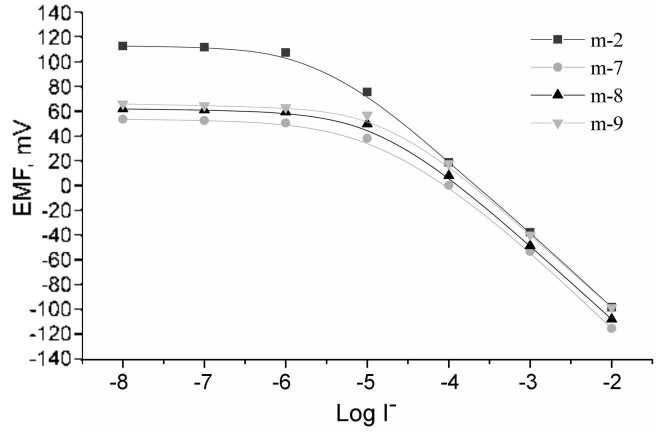

Figure 3. Potentiometric responses of the membrane prepared from different amounts of ionophore (m-2 : 1 mg, m-7 : 2 mg, m-8 : 3 mg, m-9 : 5 mg).

can be concluded that the membrane exhibits excellent response toward iodide ion in pH 5.0 buffering solution. The effect of the buffer strength was also evaluated. When the molarity of the Tris-HCl (pH 5.0) was more than 0.05 M, the buffering capacity for some strongly acidic and basic anions was satisfied within the anion concentrations tested. All remaining experiments were performed using a 0.05 M Tris-HCl of pH 5.0.

The capacity of ionophore containing in the memebranes is optimized by preparing membranes with 66 mg *o*-NPOE, 33 mg PVC, 50 mol% TDDMACl, and differing capacities of the ionophore, ranging from 1.0 to 5.0 mg. Several iodide calibrations are performed using each membrane. The potentiometric properties toward iodide ion on the capacity of ionophore in 0.05 M Tris-HCl pH 5.0 buffer solutions are also listed in Figure 3 and Table 1. In Figure 3, it was noted that the potential slope of the membranes with more than 1.0 mg ionophores (m-7, m-8, m-9) was decreased than that of the membrane with 1.0 mg ionophore (m-2). So the optimal capacity of ionophore seems to be about 1.0 mg in the PVC membrane. The response time of the ionophore-based membrane electrode ranged from less than 10 sec at all concentrations of iodide, and these novel prepared electrodes do not display any hysteresis effects. A capacity of 1.0 mg ionophore is selected for use in the preparation of all further membranes.

The effect of plasticizers used was investigated in PVC polymeric membranes containing 1.0 mg ionophore Y, 50 mol% TDDMACl *vs.* ionophore, 33 mg PVC, and 66 mg plasticizer. Figure 4 illustrates the iodide calibration curves for their electrodes in 0.05 M Tris-HCl pH 5.0 buffer solutions. Membranes prepared from *o*-NPOE showed the best detection limit, the best linear range, and Nernstian slope for iodide. *o*-NPOE was chosen as a proper plasticizer for use in the iodide-ISE membranes.

The percentage of ion-exchanger (TDDMACl) used in the membranes is optimized by preparing membranes with 66 mg *o*-NPOE, 33 mg PVC, 1 mg ionophore, and differing percentages of the additive, 0 and 50 mol% of the ionophore.

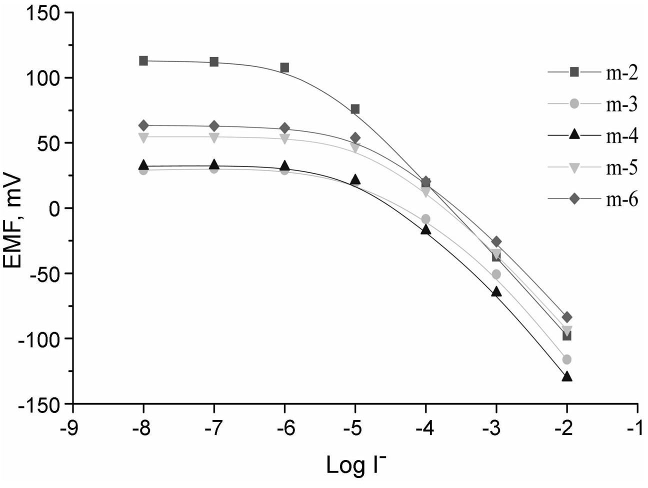

Figure 4. Potentiometric responses of the membrane prepared from different plasticizers with ionophore Y (m-2 : *o*-NPOE, m-3 : DOS, m-4 : DOP, m-5 : DOA, m-6 : DBS).

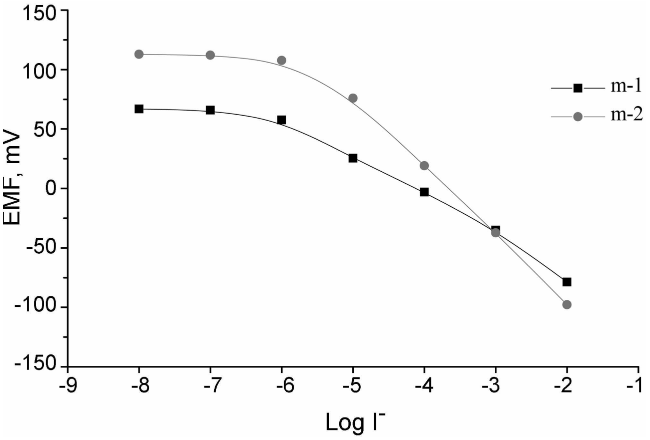

Figure 5. Potentiometric responses of the membrane including additive and none additive with ionophore.

Figure 5 shows the iodide calibration curves as a function of additive percentages in 0.05 M Tris-HCl pH 5.0 buffer solutions. The different slopes were obtained by calibrating the ISE in different additive percentages. The worsening of the detection limit and slope below 50 mol% additive may be explained by the strong influence of ion-exchanger as an additive compound. The optimal formulation is when 50 mol% is used.

The ISE based on the urea derivative exhibits a linear stable response over a wide concentration range (1.0×10^{-5} ~1.0×10^{-2}) with a slope of −57.7 mV/decade and a detection limit of $\log[I^-] = -5.63$. Among the membranes prepared from ionophore, the membrane "m-2" gives the good sensitivity and Nernstian slope. The responses of the membrane to nine interfering anions were also tested under the optimal conditions determined. The selectivity coefficients are shown in Table 2, and reflects response of the electrode to the testes with each anion in pH 5.0 buffer solutions. Although the Hofmeister series is $ClO_4^- > SCN^- > Sal^- > I^- > NO_3^- > NO_2^- > Br^- > Cl^- > F^-$, the selectivity

Table 2. Selectivity coefficients ($\log K^{pot}_{I^-,J}$) for various interfering ions for membrane (m-2) electrodes obtained by SSM

Membrane No.	Ionophore (mg)	$\log K^{pot}_{I^-,J}$								
		F^-	Cl^-	Br^-	NO_2^-	NO_3^-	I^-	Sal^-	SCN^-	ClO_4^-
m-2	1	−3.46	−3.40	−2.75	−3.13	−2.27	0	−1.05	−1.05	−1.42

series of the membrane "m-2" gives the follow as $I^- > SCN^-, Sal^- > ClO_4^- > NO_3^- > Br^- > NO_2^- > Cl^- > F^-$. This urea derivative-based ISEs exhibited excellent selectivity for iodide anion over every anion tested.

Conclusion

The potentiometric properties towards iodide anion are dependent upon buffering pH, ionophore, additive and plasticizer. Among the various membranes, the iodide-ISE prepared from urea derivative may be effectively and selectively bound with iodide anion in the polymeric membrane under the condition of pH 5.0. This membrane exhibits a linear stable response over a wide concentration range ($1.0 \times 10^{-5} \sim 1.0 \times 10^{-2}$) with a slope of −57.7 mV/decade, a detection limit of $\log[I^-] = -5.63$, and a selectivity coefficient for iodide against perchlorate anion ($\log K^{pot}_{I^-,J} = -1.42$). The selectivity series of the membrane gives the follow as $I^- > SCN^-, Sal^- > ClO_4^- > NO_3^- > Br^- > NO_2^- > Cl^- > F^-$. The membrane was found to be chemically and physically stable, and made steady potential in 10 seconds with high reproducibility.

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