

Characterization of All Solid State Hydrogen Ion Selective Electrode Based on PVC-SR Hybrid Membranes

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Received: 27 March 2003 / Accepted: 8 May 2003 / Published: 30 June 2003

Abstract: Hydrogen ion selective membranes formulated with 3140 RTV silicone rubber (SR) in PVC were studied to extend the life time of solid state ion sensors through improved membrane adhesion. All solid state hydrogen ion selective electrodes were prepared by incorporation of tridodecyl amine (TDDA) as an ionophore, potassium tetrakis[3,5-bis(p-chlorophenyl)borate (KTpClPB) as a lipophilic additive, bis(2-ethylhexyl)adipate (DOA) as a plasticizer. Their linear dynamic range was pH 2.0-11.0 and showed the near Nernstian slope of 55.1 ± 0.2 mV/pH ($r=0.999$). The influences from alkali and alkaline earth metal ions were studied for the response of the final ISE membrane composition. Impedance spectroscopic data showed that the resistance was increased by increasing SR content in PVC. Brewster Angle Microscopy (BAM) image showed clear differences according to the SR compositions in PVC. Life time of the all solid state membrane electrode was extended to about 2 months by preparing the membrane with PVC and SR. The standard reference material from NIST (2181 HEPES Free acid and 2182 NaHEPESate) was tested for the ISE and it gave a good result.

Keywords: Hydrogen ion sensor; Polymer membrane; All solid state ISE; BAM; Impedance spectroscopy

Introduction

In views of ease of preparation, low electrical resistance, and handling safety, there have been considerable interest in non glass systems for clinical pH applications [1,2]. Due to this, there has been much attention in the development of various types of solid-state electrochemical sensors (i.e., ion,

gas, and biosensors), in which polymer membranes are cast on the solid surfaces without any internal reference electrolyte solution [3-6]. Such devices could offer the advantages of miniaturization (for *in vivo* measurements), the capability of including multiple sensors on a single chips and mass fabrication for cost reduction.

Of these, poly(vinyl chloride) is the most commonly used membrane matrix for the conventional ISEs. However, attempts to use poly(vinyl chloride) (PVC) as a polymer matrix for the all solid state ion sensors have faced difficulties in long term stable response due to the poor adhesion of this material to a solid substrate surface. Leaching out of the active component and the plasticizer from the polymeric matrix causes the deterioration of the response of the electrodes and leads to limited electrode life time [7-9]. Up to date, several approaches were made to solve this problem including chemical anchoring of PVC membranes containing OH groups to an oxide surface [10,11], mechanical attachment of the membrane [12], photocuring techniques [13,14], and several other polymer materials [15-19]. Among them, SR based membranes were formulated without a plasticizer (which is owing to their low glass transition temperature), because it adhere strongly to most solid surfaces and exhibit less interference from lipophilic anions present in biological fluids. However, the application of the SR-based membranes to all solid-state ion sensors has not been so popular due in part to their high electrical resistance, which cause of slow and noisy response [20, 21].

Thus, to improve the response and the adhesion of the PVC to the solid substrate, we incorporated SR to PVC. To optimize the hydrogen ion selective electrode using this composite membrane, response, selectivity coefficient, life time and reproducibility, morphologys, and membrane resistance are investigated in various SR composition in PVC. The final ISE was examined for the standard reference sample prepared with 2181 HEPES free acid and 2182 NaHEPESate.

Experimental

Reagents

3140 RTV-silicone rubber (SR) was obtained from Dow Corning, Co (Korea). High molecular weight poly(vinyl chloride) (PVC), tridodecyl amine (TDDA) and potassium tetrakis(p-chlorophenyl)borate (KTpCIPB) were purchased from Fluka (USA). Bis(2-ethylhexyl)adipate (DOA) was purchased from Wako Chemical (Japan). Tetrahydrofuran (THF) was purchased from Kanto Chemical Co. (Japan). Analytical grade of the other chemicals were used without further purification. Standard solutions and buffers were prepared with doubly distilled water ($18 \text{ M}\Omega\cdot\text{cm}$). Standard Reference Sample, 2181 HEPES free acid and 2182 NaHEPESate were purchased from NIST (USA).

Fabrication of Hydrogen Ion Selective Membrane Electrodes

The PVC-SR membranes were prepared as follows: 160.0 mg total amount of membrane components, various compositions of TDDA, KTpCIPB, DOA, PVC, and SR were stirred magnetically in 1.6 ml of THF for 30 min. In all the experiments, 50 mol % of the lipophilic salt to ionophore was used. The ratio of PVC/plasticizer=1:2 [22] and 3140 RTV/plasticizer=77.2/21.6 [23] calculated in the weight percentage of the plasticizer when SR incorporated to PVC, while fixed the

weight percentages of TDDA and KTpCIPB. The exact weight percentages were given in Table 1. Carbon rod substrates (diameter. 4.8 mm) were dipped into the membrane solutions for 3 s (5 times), followed by evaporation of THF at room temperature (dust free) for 2 days. All electrodes were presoaked in distilled water for 24 h before the EMF measurements.

Table 1. Composition and electrochemical characteristics of PVC-SR electrodes to hydrogen ion (a) wt % (b) mol % to ionophore.

Entry Number	PVC ^a	DOA ^a	TDDA ^a	KTpCIPB ^b	SR ^a	Slope	Selectivity, logK		
							Na ⁺	K ⁺	Ca ²⁺
1	33.0	66.0	1.0	50.0	0.0	52.2	-10.1	-9.9	-11.1
2	0.0	21.5	1.0	50.0	77.0	59.9	-9.7	-9.5	-11.3
3	31.5	62.0	1.0	50.0	5.0	53.9	-10.0	-9.7	-11.1
4	29.0	59.5	1.0	50.0	10.0	55.1	-9.8	-9.7	-11.1
5	26.3	57.2	1.0	50.0	15.0	53.8	-10.0	-9.8	-11.3
6	23.5	51.5	1.0	50.0	23.5	49.2	-9.8	-10.0	-11.4

Apparatus and EMF Measurements

Potential difference between the hydrogen ion selective electrodes (ISEs) and the reference electrode was measured using a 15 channel multi pH/Ion meter (Kosentech, Co., Korea), Which the external reference electrode was an Ag/AgCl (sat'd KCl). The electrochemical cell and the electrode used for measurements composed of as follows: Ag/AgCl (sat'd KCl)/sample solution/PVC-SR membrane/carbon/Ag. Before EMF measurements, all PVC-SR membrane electrodes were calibrated with pH 4.01, 6.87, and 10.00 buffer solutions. The performance of the hydrogen ion selective PVC-SR electrodes were examined by measuring the EMF of the electrodes in the range of 2.0~11.0 which magnetically stirring. The pHs of the solutions were monitored with a glass electrode (Coring Co. USA). The response time was obtained by adding a small volume of 1.0 M HCl into a buffer solution of pH 8.5 as the background solution. All the measurements were carried out in a room temperature. Selectivity coefficients of hydrogen were determined by using the separate solution method [25] using a 100 mM solution containing the interfering ions. Membrane images of PVC-SR on the carbon substrate were obtained using Brewster Angle Microscope (BAM2plus NFT, Co., USA). The electric resistance of the PVC-SR membranes was evaluated by impedance measurements carried out in a 50 mM citrate buffer (pH 5.5) in the frequency range of 100 KHz-10 mHz. Impedance spectra were obtained using EG&G 283 potentiostat/galvanostat and EG&G Princeton Applied Research 5210 lock-in amplifier, EG&G 398 software. The pH of the standard reference sample 0.05 mol/kg with respect to 2181 HEPES Free acid and 2182 NaHEPESate was measured.

Results and Discussion

Potentiometric Response of PVC-SR Electrodes

Potentiometric responses of hydrogen ion selective electrodes (ISEs) based on PVC-SR matrix were

examined at the first stage. 50 mol % of KTpCIPB to TDDA was used in subsequent experiments as described in the experimental, because, there were many reports that monovalent ion using 50 mol % of lipophilic salt to ionophore, and most of cation selective neutral carrier membranes contain small controlled amounts of alkali salts with lipophilic anions, e.g. KTpCIPB. It has been well known that the incorporation of such salts have proved to decrease anion interference, lower the membrane resistance, improve electrical properties, and enhance the selectivity characteristics by increasing the cation extraction efficiency. Figure 1 shows the potential variation according to pH using hydrogen ion selective electrodes based on PVC-SR membranes containing TDDA as a ionophore, KTpCIPB as a lipophilic additive, and DOA as a plasticizer, PVC-SR as a matrix.

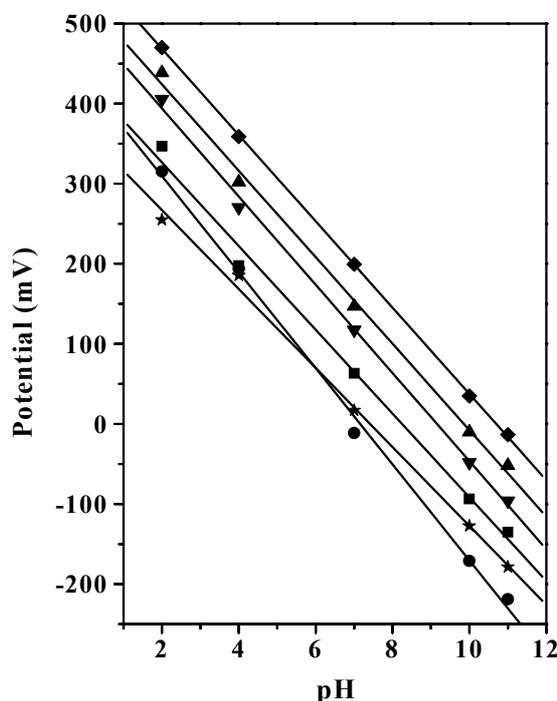


Figure 1. Calibration curves for the PVC-SR membrane electrodes. ■ PVC ▲ 5.0 wt % ▼ 10.0 wt % ◆ 15.0 wt % ★ 23.5 wt % ● SR.

The exact weight percentages of PVC-SR membrane were listed in Table 1. As shown in Table 1, all the electrodes based on PVC-SR membranes showed near-Nernstian slope in pH 2.0-11.0. The electrode of no.1 based on PVC showed near-Nernstian slope of 52.2 ± 0.2 mV/pH ($r=0.997$) in pH 2.0-11.0 may be due to weak adhesion. The electrode of no.2 based on SR showed a non linear slop, $pH > 7; 68.9$ mV/pH, $pH < 7; 48.7$ mV/pH. Moreover, the response time is long because of the high resistance need long time curing. To improve the response of the electrode, SR incorporated to PVC. When increasing the composition of SR in PVC, the slope of the electrode became increased. The electrode of no.3 based on 5.0 wt % of SR in PVC showed the near-Nernstian slope of 53.9 ± 0.2 mV/pH ($r=0.998$) in pH 2.0-11.0. The electrode of no.4 based on 10.0 wt % of SR in PVC also showed the near-Nernstian slope of 55.1 ± 0.2 mV/pH ($r=0.999$) in pH 2.0-11.0. However, the composition of the SR was higher than 10.0 wt %, the slope gradually decreased. The electrode of no.5 based on 15.0

wt % of SR in PVC showed the near-Nernstian slope of 53.8 ± 0.3 ($r=0.999$) mV/pH in pH 2.0-11.0. The electrode of no.6 based on 23.5 wt % of SR in PVC showed the sub-Nernstian slope of 49.2 ± 0.3 mV/pH ($r=0.998$) in pH 2.0-11.0. When measuring the pHs of the solutions were monitored with a glass electrode to compare the membrane electrode based on PVC-SR. In the same experimental condition, the standard deviation of the electrode of no.4 based on 10.0 wt % of SR in PVC was 2.7 % when measured 5 times.

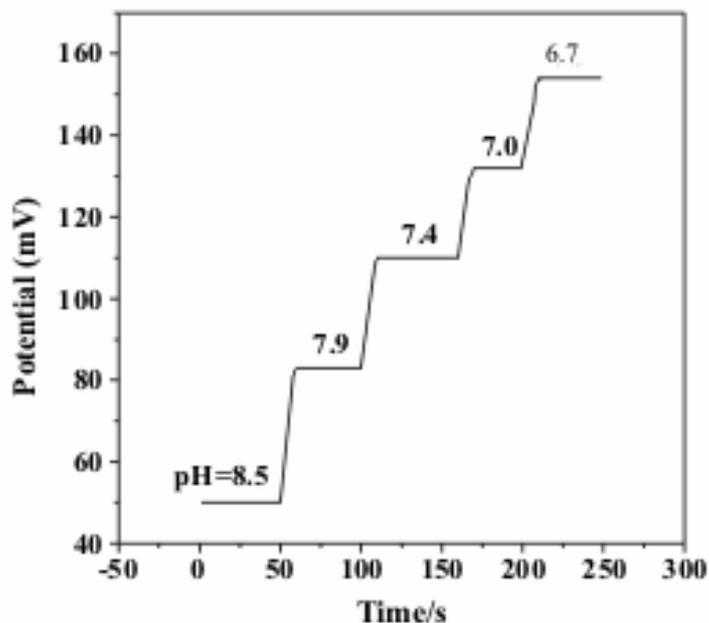


Figure 2. Response of the membrane electrode based on 10.0 wt % SR in PVC to an injection of 1.0 M HCl into a buffer solution of pH 8.5 as the background solution.

In order to evaluate the response time, the membrane electrode based on 10.0 wt % SR in PVC was conditioned in the distilled water 1h before measuring. The response times for the electrode based on PVC-SR were measured by adding a small volume of a 1.0 M HCl to a rapidly stirred buffer solution of pH 8.5 as the ion background solution. Figure 2 shows response curve of ISE. In the pH range from pH 8.5 to 6.7, the rate of response decreased when the SR content in PVC increased. This might be due to high resistance of SR [20, 21]. As shown in Figure 2, the response time ($t_{90\%}$) of the electrode based on 10.0 wt % of SR in PVC was less than 10 s in all cases.

The stability and reproducibility of the membranes were evaluated by comparing the slopes from periodic calibrations in the range pH 2.0-11.0. The variation of PVC-SR electrodes in the response slope of several measured every 5 days for 60 days. From the results can be seen, the slope of no.1 electrode was reduced after 35 days and the electrode seems to lose the ability of hydrogen ion selective electrode. This may be due to the weak adhesion of PVC only to the solid state electrode. Compared to this, the electrodes based on 5.0 wt %, 10.0 wt %, 15.0 wt, and 23.5 wt % of SR in PVC were showed reproducible slope. Life time of electrode of no.4 was 2 months. From this, it can be

concluded that this phenomenon is due to increasing the adhesion to the solid state electrode. However, the resistance of the electrode was increased when SR was incorporated into the PVC matrix.

The Surface Morphology According to SR Contents

The morphology of the membrane surfaces based on various PVC-SR compositions coated on the carbon substrate was observed with Brewster Angle Microscope (BAM). Figure 3a showed an image for the PVC membrane, it showed smooth surface without any large apparent pores, while figure 3b obtained for just SR layer showed big pore sizes. Figure 3c showed an image for the membrane based on 5.0 wt % of SR in PVC, it showed the pore was bigger than the one of the PVC membrane. Figure 3d showed an image for the membrane based on 10.0 wt % SR in PVC, it showed the pore sizes became smaller and a little aggregate. Figure 3e showed an image for the membrane based on 15.0 wt % of SR in PVC, it showed aggregation of the polymer and the surface of the membrane was very rough. Figure 3f showed an image for the membrane based on 23.5 wt % of SR in PVC, it showed aggregation of the polymer and the surface of the membrane was rougher than the membrane based on 15.0 wt % of SR in PVC. As shown in Figure 3 (a-f), the pore sizes of the PVC-SR membrane were increased by increasing SR content in PVC matrix and the surface became rougher because of aggregation of PVC and SR.

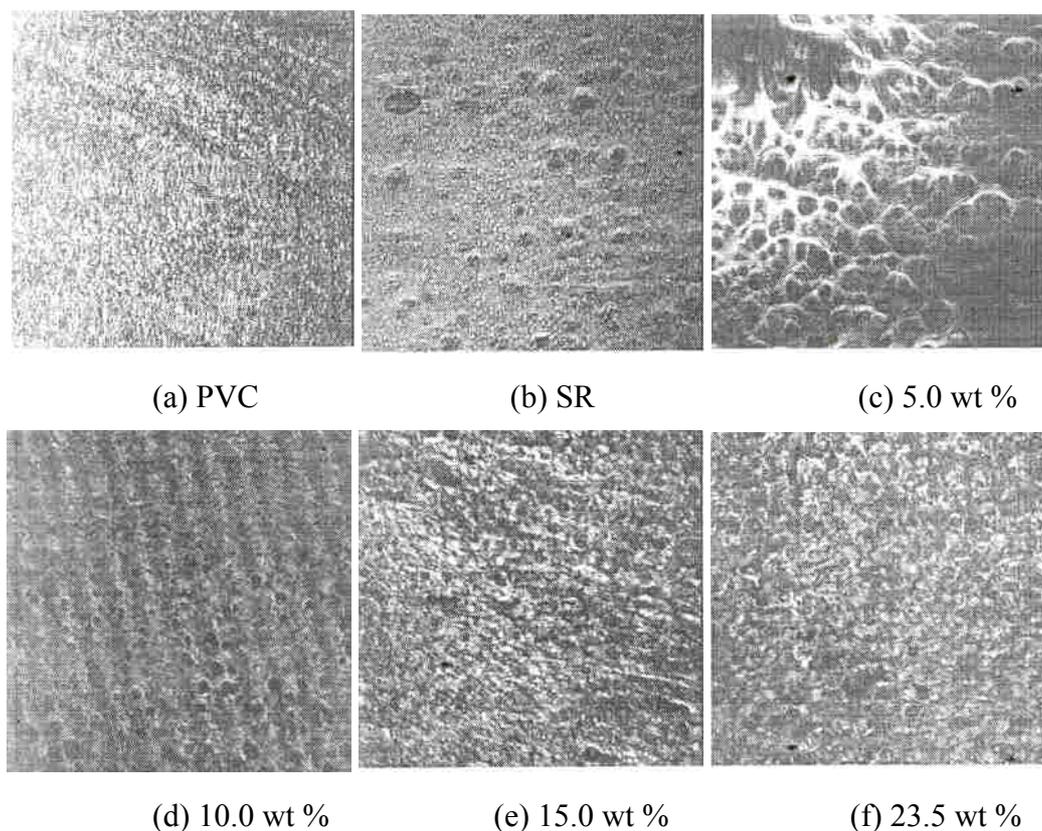


Figure 3. BAM images of the membrane based on the PVC-SR coated on carbon surfaces.

Impedance Spectra of PVC-SR Membrane Coated Electrode

To understand the interface phenomena of the PVC-SR membrane electrode, impedance spectra

were obtained. The impedance spectrum of the PVC-SR membrane electrode recorded at the open circuit voltage at 5 mV in a 50 mM citrate (pH 5.5) buffer solution in the frequency range of 100 KHz-10 mHz. displayed an arc and a normal line to the x-axis in the regions of high and low frequencies, respectively, as shown in Figure 4a. The arc in the high frequency corresponds to which in parallel with electrode capacitance (CPE1) and a PVC-SR membrane resistance (R1). The line in the low frequency was attributed to a Warburg impedance (CPE2), that is associate with the diffusion of hydrogen ion through the PVC-SR membrane. The complex impedance data which reported in Figure 4a were fitted by equivalent circuits using Z View2 program of Scribner Associates Inc [25]. Figure 4b showed the equivalent circuit of Figure 4a, all the PVC-SR membrane impedance result fitted by this equivalent circuit. Table 2 showed the parameter values of the equivalent circuit for the impedance spectrum of a hydrogen selective electrode based on PVC-SR membrane. Impedance spectrums for all the PVC-SR membrane electrode in various content of SR in PVC with variation from 0.0 wt % to 23.5 wt % showed small differences in the resistance values. The resistances of the membrane were $4.2 \times 10^4 \Omega$ for the membrane based on PVC, $1.5 \times 10^5 \Omega$ for 5.0 wt %, $3.5 \times 10^5 \Omega$ for 10.0 wt %, $8.0 \times 10^5 \Omega$ for 15.0 wt %, and $2.8 \times 10^6 \Omega$ for 23.5 wt % SR in PVC, respectively. As shown in Figure 4a and Table 2, the resistance of PVC-SR membranes gradually increases as the SR content in PVC increase from 0.0 wt % to 23.5 wt %. Because the resistance of liquid membrane based on SR is high [17].

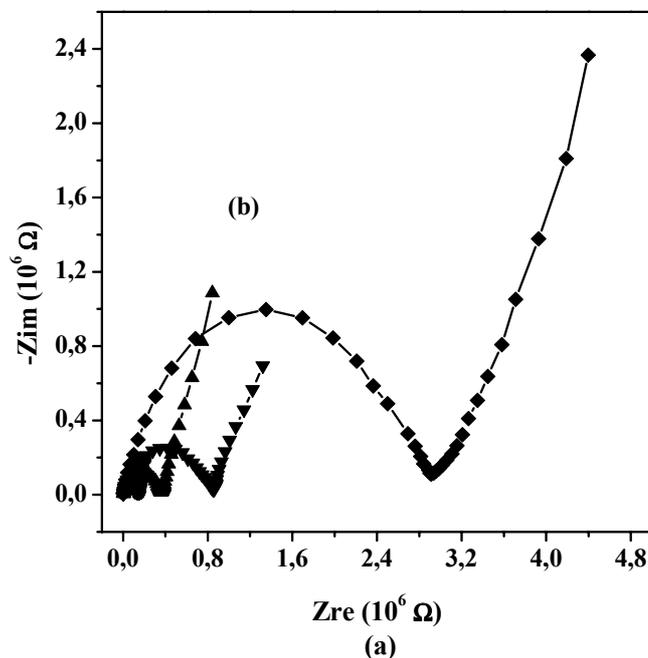


Figure 4. (a) Impedance spectra obtained for the PVC-SR membrane electrodes in a 50 mM citrate pH 5.5 buffer in the frequency range of 100 KHz-10 mHz (■ PVC ● 5.0 wt % ▲ 10.0 wt % ▼ 15.0 wt % ◆ 23.5 wt %.), and (b) Equivalence circuit used to model the behaviors of impedance spectra reported in Figure 4(a).

Table 2. Values of the parameters of the equivalent circuit simulated for PVC-SR film.

	R1 (Ω)	CPE1		CPE2		X^{2d}
		Y_0^b (Ω^{-1})	n	Y_0^b (Ω^{-1})	n	
PVC	4.2×10^4	9.1×10^{-9}	0.84	1.0×10^{-5}	0.67	4.9×10^{-4}
5.0 wt %	1.5×10^5	2.8×10^{-10}	0.84	7.4×10^{-6}	0.75	5.1×10^{-4}
10.0 wt %	3.5×10^5	3.3×10^{-10}	0.83	4.6×10^{-6}	0.71	5.7×10^{-4}
15.0 wt %	8.0×10^5	5.7×10^{-10}	0.79	4.6×10^{-6}	0.58	3.6×10^{-4}
23.5 wt %	2.8×10^6	3.5×10^{-10}	0.83	2.8×10^{-6}	0.55	4.7×10^{-4}

Selectivity Coefficients and Real Sample Analysis

The selectivity coefficients were determined by the mixed solution method [24] in 1.0×10^{-2} M solutions of calcium chloride salts and in 1.0×10^{-1} M solution of lithium, sodium, potassium chloride salts. The selectivity coefficients were calculated by the following equation. $K_{A,B} = (C_A)^{Z_B} / (C_B)^{Z_A}$, $K_{A,B}$ was selectivity coefficient, C_A and C_B were concentration of hydrogen ion and interfering ion. Z_A and Z_B were charges of hydrogen and interfering ions.

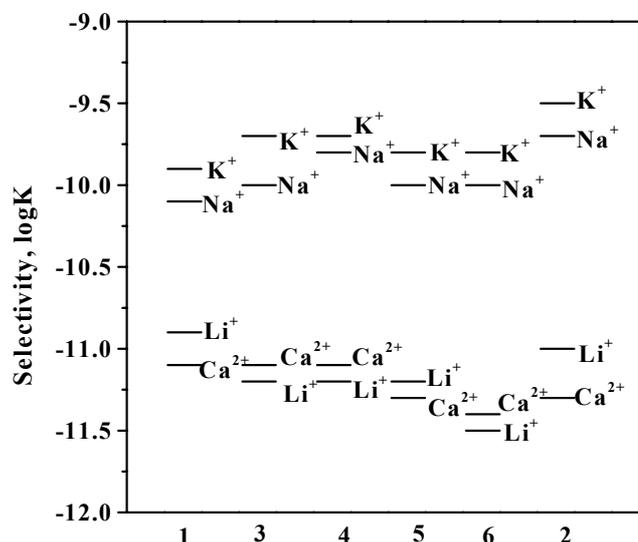


Figure 5. The selectivity coefficients expressed as logK of ISEs based on 1-6 (Numbers 1-6 correspond to the entry numbers in Table 1) for H⁺ over other cations using the mixed solution method at 10^{-2} M calcium ion and 10^{-1} M of lithium, sodium, potassium ions as interfering ions.

Figure 5 shows the selectivity coefficient diagram for the hydrogen ion of the ISEs based on PVC, 5.0 wt % of SR in PVC, 10.0 wt % of SR in PVC, 15.0 wt % SR in PVC, 23.5 wt % of SR in PVC, and SR matrix. The selectivity coefficients of the ions in logarithmic values of membrane which SR

incorporated in PVC for K and Na were higher than the PVC membrane. The selectivity coefficients of the ions in logarithmic values of the electrode based on 10.0 wt % of SR in PVC are as follows: K = -9.7, Na = -9.8, Li = -10.9, Ca = -11.1. It shows that hydrogen ion selective membrane electrode based on 10.0 wt % of SR in PVC that has high selectivity for hydrogen over many cations especially relative to Ca^{2+} , which is usually present in real samples.

The pH of the standard reference sample 0.05 mol/kg with respect to 2181 HEPES Free acid and 2182 NaHEPESate was measured by a glass electrode at pH 7.54, pH of the standard reference sample measured by the sensor which containing 10.0 wt % SR showed pH 7.55, 7.54, 7.54, 7.53, and 7.52 when measured 5 times, so the pH was determined to be 7.54 ± 0.02 .

Conclusion

When SR was incorporated into the PVC matrix, the adhesion of membranes to the solid electrode was increased. Thus, the life time of the ISE became much longer than the PVC membrane. Especially, the electrode containing 10.0 wt % SR in the PVC matrix showed the near-Nernstian slope of 55.1 mV/pH in pH 2.0-11.0, and showed high selectivity over the other cations and gave fast response that can be comparable to the PVC membrane electrode. The pore sizes and roughness of the PVC-SR membrane were increased by increasing the SR content in PVC. The resistance of PVC-SR membranes was also increased by increasing the SR content in PVC. The life time of the membrane was 2 months. For sensor with optimized membrane composition, the relative standard deviation was 2.7 %.

Acknowledgment

This study was supported by a grant of the Korea Health 21 R&D Project (03-PJ1-PG1-21400-0001), Ministry of Health & Welfare, South Korea.

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Sample Availability: Available from the authors.

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