

One-Component Room Temperature Vulcanizing-Type Silicone Rubber-Based Calcium-Selective Electrodes

Bong Kyun Oh, Chang Yong Kim, Hyun Jung Lee, Kyung Lae Rho, Geun Sig Cha, and Hakhyun Nam*

Department of Chemistry and Research Institute of Basic Science, Kwangwoon University, 447-1 Wolgye-Dong, Nowon-Ku, Seoul 139-701, Korea

New calcium-selective membranes for all-solid-state ion sensors are developed with a highly adhesive one-component room temperature vulcanizing-type silicone rubber (RTV-1-type SR) matrix. The membranes are formulated with 21.6 wt % bis(2-ethylhexyl) adipate, 0.3 wt % tetradodecylammonium tetrakis(*p*-chlorophenyl)borate (ETH 500), 0.1 wt % potassium tetrakis(*p*-chlorophenyl)borate, and 0.8 wt % calcium-selective neutral carrier ETH 129 or ETH 1001. Plasticizer added to the RTV-1-type SR matrix not only decreases the bulk membrane resistance but also increases the solubility of electroactive components incorporated in the membrane without significantly deteriorating its adhesive strength. It is found that the lipophilic salt ETH 500 remarkably enhances the calcium selectivity of ETH 129 or ETH 1001 ligands in the SR matrix; the selectivity coefficients ($K_{Ca^{2+},j}^{pot}$ by separate solution method, where $j = Li^+, Na^+, K^+$, or Mg^{2+}) for the optimized membranes were below 10^{-5} . Potentiometric characteristics of planar-type Ag electrodes coated with optimized RTV-1-type SR membranes, e.g., response slope 29.0 ± 0.5 mV/decade, detection limit below 5.0×10^{-7} M $a_{Ca^{2+}}$, and 2–3 mV of potential drift per day, were virtually the same as those of the corresponding poly(vinyl chloride) membrane-based conventional electrodes, but with greatly enhanced sensor-to-sensor reproducibility and lifetime (3–9 weeks).

Ion-selective electrodes (ISEs) based on plasticized poly(vinyl chloride) (PVC) membranes doped with neutral carriers are now routinely used for the determination of potassium, sodium, calcium, chloride, and carbonate ions in blood, urine, and other physiological fluids.^{1–3} However, the use of PVC-based membranes in all-solid-state ion sensors [e.g., coated-wire electrodes (CWEs) and ion-selective field effect transistors (ISFETs)] resulted in limited success because of their inherently weak adhesion to most solid surfaces. Several alternative methods have been proposed to solve such problems: some examples include the modification of the PVC matrix for binding to hydroxyl-bearing solid surfaces,^{4–6} mechanical fastening of the membranes,⁷ chemi-

cal attachment of sensing membranes to solid surfaces,^{8–12} and use of adhesive polymer matrices other than PVC.^{13–20} In many cases, however, those methods, even if they improve membrane adhesion and lifetime, were hardly practical, as they are too sophisticated to be employed for mass fabrication or result in poor electrochemical performance. Thus, design of solvent polymeric ion sensing membranes that are easily applicable on any all-solid-state device without compromising their potentiometric performance is a prerequisite in developing microfabricated ion-selective sensor arrays.

In recent years, we have attempted to develop a new class of ion-selective membranes employing a highly adhesive one-component room temperature vulcanizing-type silicone rubber (RTV-1-type SR) matrix for all-solid-state ion sensors.²⁰ Silicone rubber (SR)-based membranes have attracted some attention from the early days of ISE research:^{18–30} unlike PVC, SR-based membranes may be formulated without plasticizer (owing to their

- (6) Cosofret, V. V.; Erdoesy, M.; Buck, R. P.; Kao, W. J.; Andersone, J. M.; Lindner, E.; Neuman, M. R. *Analyst* **1994**, *119*, 2283–2292.
- (7) Blackburn, G.; Janata, J. *J. Electrochem. Soc.* **1982**, *129*, 2580–2584.
- (8) Battilotti, M.; Colilli, R.; Giannini, I.; Giongo, M. *Sens. Actuators* **1989**, *17*, 209–215.
- (9) Jaffrezic-Renault, N.; Chovelon, J. M.; Perrot, H.; LePerchec, P.; Chevalier, Y. *Sens. Actuators B* **1991**, *5*, 67–70.
- (10) Sudholter, E. J. R.; van der Wal, P. D.; Skowronska-Ptasinska, M.; van den Berg, A.; Bergveld, P.; Reinhoudt, D. N. *Sens. Actuators* **1989**, *17*, 189–184.
- (11) Sudholter, E. J. R.; van der Wal, P. D.; Skowronska-Ptasinska, M.; van den Berg, A.; Bergveld, P.; Reinhoudt, D. N. *Anal. Chim. Acta* **1990**, *230*, 59–65.
- (12) Brunink, J. A. J.; Lugtenberg, R. J. W.; Brozka, Z.; Engebersen, J. F. J.; Reinhoudt, D. N. *J. Electroanal. Chem.* **1994**, *378*, 185–200.
- (13) Cha, G. S.; Liu, D.; Meyerhoff, M. E.; Cantor, H. C.; Midgley, A. R.; Goldberg, H. D.; Brown, R. B. *Anal. Chem.* **1991**, *63*, 1666–1672.
- (14) Wakida, S.-I.; Yamane, M.; Higashi, K.; Hiroy, K.; Ujihara, Y. *Sens. Actuators B* **1990**, *1* (1–6), 412–415.
- (15) Johnson, S.; Moody, G. J.; Thomas, J. D. R. *Anal. Proc.* **1990**, *27*, 79–81.
- (16) Cha, G. S.; Brown, R. B. *Sens. Actuators B* **1990**, *1*, 281–285.
- (17) Cunningham, L.; Freiser, H. *Anal. Chim. Acta* **1986**, *180*, 271–279.
- (18) van der Wal, P. D.; Skowronska-ptasinska, M.; van den Berg, A.; Bergveld, P.; Sudholter, E. J. R.; Reinhoudt, D. N. *Anal. Chim. Acta* **1990**, *231*, 41–52.
- (19) (a) Kimura, K.; Mutsaba, T.; Tsujimura, Y.; Yokoyama, M. *Anal. Chem.* **1992**, *64*, 2508–2511. (b) Tsujimura, Y.; Yokoyama, M.; Kimura, K. *Anal. Chem.* **1995**, *67*, 2401–2404.
- (20) Shin, J. H.; Sakong, D. S.; Nam, H.; Cha, G. S. *Anal. Chem.*, in press.
- (21) van der Wal, P. D.; Sudholter, E. J. R.; Boukamp, B. A.; Bouwmeester, H. J. M.; Reinhoudt, D. N. *J. Electroanal. Chem.* **1991**, *317*, 153–168.
- (22) Lindner, E.; Niegriesz, Z.; Toth, K.; Pongor, E.; Berube, T. R.; Buck, R. P. *J. Electroanal. Chem.* **1989**, *259*, 67–80.
- (23) Mostert, I. A.; Anker, P.; Jenny, H.-B.; Oesch, U.; Morf, W. E.; Ammann, D.; Simon, W. *Microchim. Acta* **1985**, *33*–38.
- (24) Anker, P.; Jenny, H.-B.; Wuthier, U.; Asper, R.; Ammann, D.; Simon, W. *Clin. Chem.* **1983**, *7*, 1447–1448.

- (1) Oesch, U.; Amman, D.; Simon, W. *Clin. Chem.* **1986**, *32*, 1448–1459.
- (2) Arnold, M. A.; Meyerhoff, M. E. *Anal. Chem.* **1984**, *56*, 20R–48R.
- (3) Davies, M. L.; Hamilton, C. J.; Murphy, S. M.; Tighe, B. J. *Biomaterials* **1992**, *13*, 971–978.
- (4) Satchwill, T.; Harrison, D. J. *J. Electroanal. Chem.* **1986**, *202*, 75–81.
- (5) Moody, G. J.; Thomas, J. D. R.; Slater, J. M. *Analyst* **1988**, *113*, 1703–1707.

low glass transition temperature), adhere strongly to most solid surfaces, and exhibit less interference from lipophilic anions present in biological fluids. However, the application of SR-based membranes to all-solid-state ion sensors has not been so popular, due in part to their high electrical resistance, the cause of slow response and noisy signal.^{21,22} Furthermore, most electroactive compounds are not compatible with the SR matrix, and the resultant membranes exhibit either irreproducible or negligible potentiometric responses: only a few neutral carriers, such as valinomycin, certain calix[4]arene derivatives, and nonactin, are known to exhibit the same degree of ion carrying ability in the SR matrix as in the highly plasticized PVC matrix.^{19,21–23} These problems prompted us to consider the use of an appropriate plasticizer and lipophilic salts for the SR matrix in order to lower its electrical resistance and to help uniform dissolution of electroactive components in the resulting membrane.²⁰

In this contribution, we describe the effects of various electroactive components, i.e., plasticizer, lipophilic additives, and ionophores, incorporated in RTV-1-type SR membranes on their potentiometric properties. To this end, a series of calcium-selective SR membranes formulated with varying amounts of bis-(2-ethylhexyl) adipate or bis-(2-ethylhexyl) sebacate plasticizer, tetradodecylammonium tetrakis(*p*-chlorophenyl)borate, potassium tetrakis(*p*-chlorophenyl)borate, and a calcium-selective neutral carrier (ETH 129 or ETH 1001) were first tested in conventional ISEs and subsequently applied on planar-type CWs. It will be shown that the sensors with calcium-selective membranes developed in this study exhibit much better sensor-to-sensor reproducibility, high calcium selectivity, improved potential stability, and longer lifetime compared to those prepared with PVC-based membranes or other elaborate techniques.

EXPERIMENTAL SECTION

Reagents. The 3140 RTV silicone rubber (SR) was a product of Dow Corning Co. (Midland, MI), while poly(vinyl chloride) (PVC), diethyl *N,N'*-[(4*R*,5*R*)-4,5-dimethyl-1,8-dioxo-3,6-dioxaoctamethylene]bis(12-methylaminododecanoate) (ETH 1001), *N,N,N',N'*-tetracyclohexyl-3-oxapentanediamide (ETH 129), bis-(2-ethylhexyl) adipate (DOA), bis-(2-ethylhexyl) sebacate (DOS), potassium tetrakis(*p*-chlorophenyl)borate (KTpCIPB), and tetradodecylammonium tetrakis(*p*-chlorophenyl)borate (TDATpCIPB, ETH 500) were purchased from Fluka Chemie AG (Buch, Switzerland). Tris(hydroxymethyl)aminomethane (Tris) was obtained from Sigma Chemical Co. (St. Louis, MO). All other chemicals used were analytical-reagent grade. Standard solutions and buffers were prepared with deionized water.

Preparation of Ion-Selective Membranes. PVC-based calcium-selective membranes were prepared by incorporating ETH 129 or ETH 1001 into the plasticized PVC matrices; their

Table 1. Composition of Silicon Rubber-Based Calcium-Selective Membranes^a

type	no.	SR	ETH 129	ETH 1001	DOA	DOS	KTpCIPB ^b	ETH 500 ^b
I	1	99.0	1.0					
	2	98.0	1.0				1.0 (46.4)	
	3	99.0		1.0				
	4	98.0		1.0			1.0 (69.0)	
II	5	78.0	0.8		21.2			
	6	78.0	0.8			21.2		
	7	77.9	0.8		21.2		0.1 (14.0)	
	8	78.0		0.8		21.2		
III	9	77.2	0.8		21.6		0.1 (14.0)	0.3 (14.0)
	10	77.2		0.8	21.6		0.1 (21.0)	0.3 (21.0)

^a In wt %. ^b Mol % relative to the ionophore is given in parentheses.

compositions (33 wt % PVC, 65.4 wt % NPOE or DOS, 1 wt % ionophore, and 0.6 wt % KTpCIPB) have been optimized as described in the literature.^{32,33} Various 3140 RTV SR-based membranes were prepared by dissolving 198 mg of silicone rubber, 2 mg of calcium-selective neutral carrier (ETH 129 or ETH 1001), and varying amounts of plasticizer (0–90 μ L of DOA or DOS) and lipophilic additives (0–0.54 mg of KTpCIPB, 0.7 mg of TDATpCIPB) in 0.4 mL of THF; their exact compositions in weight percent are given in Table 1. All membrane cocktails were either cast in glass rings placed on Teflon plates for conventional ion-selective electrodes or directly deposited on planar-type silver electrodes. PVC membrane cocktails were dried for at least 24 h, while those based on 3140 RTV SR were dried for 2–4 days at room temperature.

EMF Measurements. Initial evaluations of the electrochemical properties of the membranes were made using conventional ISEs. Small disks were punched from the cast films and mounted in Philips electrode bodies (IS-561; Glasblaserei möller, Zürich, Switzerland). For all electrodes, 0.1 M CaCl₂ was used as an internal filling solution. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference electrode (Model 90-02). The potential difference between the ISEs and the reference electrode was measured using an IBM AT-type computer equipped with a home-made high-impedance input 16-channel analog-to-digital converter. The dynamic response curves were obtained by adding standard solutions to 200 mL of magnetically stirred background electrolyte (0.05 M Tris-HCl, pH 7.2) every 100 s to vary the concentrations of primary ions (Ca²⁺, Mg²⁺, K⁺, Li⁺, and Na⁺) stepwise from 10^{−6} to 10^{−1} M, and the emf values were measured every second at room temperature. Membrane resistance was estimated according to the method of Diamond and Regan.³⁴

Activity coefficients were calculated according to the modified Debye–Hückel equation proposed by Robinson and by Guggenheim and Bates.³⁵ The ionic strength of 0.05 M Tris-HCl buffer (pH 7.2) was calculated according to the method described in the

(25) Ammann, D.; Anker, P.; Jenny, H.-B.; Simon, W. In *Analytical Chemistry Symposia Series Vol. 8*; Pungor, E., Ed.; Elsevier Scientific Publishing Co.: Amsterdam, 1981; pp 179–184.

(26) Pick, J.; Toth, K.; Pungor, E.; Vasak, M.; Simon, W. *Anal. Chim. Acta* **1973**, *64*, 477–480.

(27) Nanjo, M.; Rohm, J. T.; Guilbault, G. G. *Anal. Chim. Acta* **1975**, *77*, 19–27.

(28) Guilbault, G. G.; Brignac, P. J. *Anal. Chem.* **1969**, *41*, 1136–1138.

(29) Fogt, E. J.; Cahalan, P. T.; Jevne, A.; Schwinghammer, M. A. *Anal. Chem.* **1985**, *57*, 1155–1157.

(30) Mascini, M.; Marrazza, G. *Anal. Chim. Acta* **1990**, *231*, 125–128.

(31) Ammann, D.; Pretsch, E.; Simon, W. *Anal. Chim. Acta* **1985**, *171*, 119–129.

(32) Anker, P.; Wieland, E.; Amman, D.; Dohner, R. E.; Asper, R.; Simon, W. *Anal. Chem.* **1981**, *53*, 1970–1974.

(33) Schefer, U.; Amman, D.; Pretsch, E.; Oesch, U.; Simon, W. *Anal. Chem.* **1986**, *58*, 2282–2285.

(34) Diamond, D.; Regan, F. *Electroanalysis* **1990**, *2*, 113–117.

(35) Dean, J. A. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill: New York, 1992; Section 8.1.

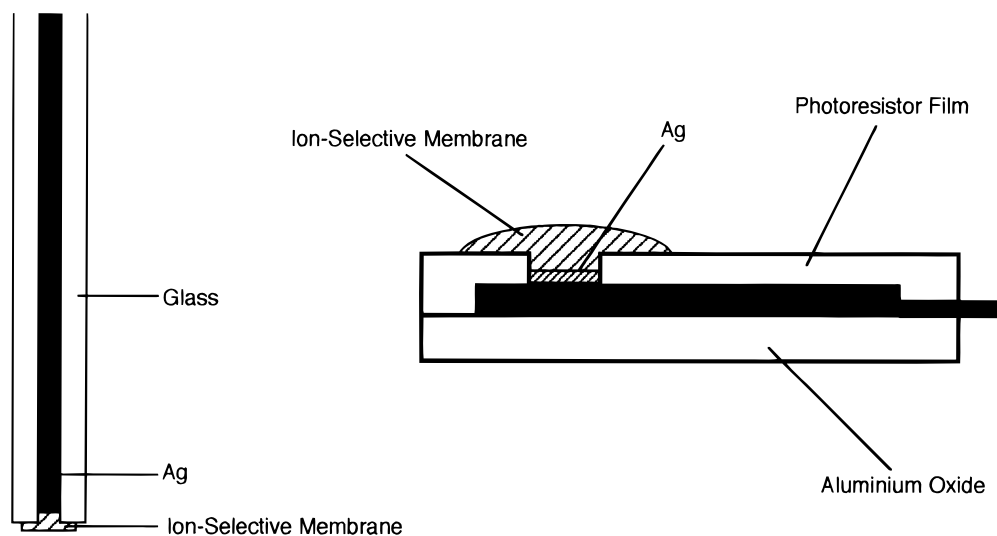


Figure 1. Schematic drawing of all-solid-state ion sensors: (A, left) wire type and (B, right) planar type.

ref 36. Selectivity coefficients, $K_{Ca^{2+},j}^{pot}$ ($j = Li^+, Na^+, K^+$, and Mg^{2+}), up to 1.0×10^{-5} were determined by the separate solution method (SSM II).^{37,38} The fixed-interference selectivity coefficient for calcium in the presence of 100 mM sodium was obtained from calibration plots according to the IUPAC recommendation.³⁸ Detection limits were estimated at the intersection of two linear lines, the one extrapolated from a high concentration range (10^{-4} – 10^{-2} M Ca^{2+}) and the other parallel to the x -axis drawn through the mean potential value of the lowest Ca^{2+} concentration employed (10^{-6} M for membranes 1–8, and 10^{-8} M for membranes 9 and 10).

Both PVC- and 3140 RTV SR-based calcium-selective membranes were also applied on the two types of silver electrodes (modified CWs; area, 0.8 mm^2) designed in our laboratory (Figure 1). A small volume of membrane cocktail solution, typically $5 \mu\text{L}$, was placed on the planar-type Ag electrode with a microsyringe. Wire-type CWs were dipped into the cocktail solution 5 times. To see the sensor-to-sensor reproducibility, several CWs were prepared from the same cocktail solution for each set of experiment. These electrodes were dried in the atmosphere for 2–4 days. All electrochemical evaluation of these CWs employed the same experimental methods as described for conventional electrodes.

RESULTS AND DISCUSSION

Evaluation of RTV-1-Type SR-Based Calcium-Selective Membranes. Most silicon rubbers commonly used in the preparation of ion-selective membranes have been two-component room temperature vulcanizing-type silicone rubbers (RTV-2-type SR), such as Siloprene K-1000, a silanol-terminated poly(dimethylsiloxane), which require additional cross-linking agent (e.g., Siloprene Vernetzer KA-1) to initiate the polymerization process.^{21–27} On the other hand, the SR matrix employed in this study is Dow Corning 3140 RTV SR (hereafter, abbreviated as SR), a methanol-

evolving-type one-component adhesive/sealant. The polycondensation reaction of this siloxane, which is activated by the moisture in the atmosphere and the titanium catalyst contained in the product, results in a clear and flexible membrane at room temperature.¹⁸

To investigate the effect of plasticizers and lipophilic salts on the potentiometric properties of SR-based calcium-selective membranes, three different types of SR membranes were prepared: type I (membranes 1–4) denotes the plasticizer-free membranes; type II (membranes 5–8) is the plasticized SR membranes; and type III (membranes 9 and 10) contains an additional lipophilic salt, TDATpCIPB (ETH 500), in plasticized SR membranes. Compositions of these membranes are given in Table 1. Although the amount of plasticizers was varied from 10 to 35 wt % in the experiment, only the type II membranes, containing about 20 wt % plasticizers, are listed in the table for the sake of clarity. The potentiometric properties of these membranes were evaluated first with conventional electrodes and further with CWs.

As can be seen from the dynamic response curve A in Figure 2, the ETH 129-based type I membrane (membrane 1) exhibits a very slow response ($t(\Delta E/\Delta t) = 40 \text{ s}$) to step titrations, which may be attributable to the high resistance of the membrane. If the slow interfacial ion exchange kinetics contributes to high surface resistance, incorporation of lipophilic anionic sites, such as KTPCIPB , into the membrane may improve the potentiometric behavior.^{22,38} However, the addition of KTPCIPB to membrane 1 resulted in a much poorer response (curve B in Figure 2). It is possible that the electrochemical properties of KTPCIPB or the neutral carriers may have been altered by chemically active siloxane medium during the curing period. In general, except for the valinomycin-based electrode, addition of KTPCIPB to nonplasticized SR membranes tends to deteriorate their electrochemical performance. Although the use of a more lipophilic ionic additive {e.g., potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB)} may treat such problems,³⁹ we have not pursued such a possibility further. Instead, we attempted to modify the SR matrix by incorporating an appropriate solvent mediator. It was also noticed that the type I membranes containing ETH 129

(36) Perin, D. D.; Dempsey, B. *Buffers for pH and Metal Ion Control*; Chapman and Hall: London, 1974; Chapter 5.

(37) Gadzekpo, V. P. Y.; Christian, G. D. *Anal. Chim. Acta* **1984**, *164*, 279–282.

(38) (a) IUPAC Recommendations for Nomenclature of Ion-Selective Electrodes. *Pure Appl. Chem.* **1994**, *66*, 2527–2536. (b) IUPAC Selectivity Coefficients for Ion-Selective Electrodes: Recommended Methods for Reporting $K_{A,B}^{pot}$ values. *Pure Appl. Chem.* **1995**, *67*, 507–518.

(39) Rosatzin, T.; Bakker, E.; Suzuki, K.; Simon, W. *Anal. Chim. Acta* **1993**, *280*, 197–208.

Table 2. Electrochemical Properties of Silicone Rubber-Based Calcium-Selective Membranes

type	no.	slope (mV/decade) ^a	detection limit (log $a_{Ca^{2+}}$)	$\log K_{Ca^{2+},j}^{Pot}$				membrane resistance (M Ω)
				$j = Na^+$	$j = K^+$	$j = Mg^{2+}$	$j = Li^+$	
I	1	41.0		-2.61	-2.73	-2.88	-2.16	>2000
	2							>2000
	3							>2000
	4							>2000
II	5	44.0	<-6.00	-2.10	-3.63	-4.41	-2.17	200-220
	6	39.6		-2.40	<-5.00	<-5.00	-1.80	1100-1200
	7	28.8		-3.80	-4.70	-3.10	-2.30	150-200
	8	27.4		-0.06	-0.64	-5.00	-0.41	600-900
III	9 ^b	28.3 \pm 0.5	-6.57 \pm 0.32	<-5.00	<-5.00	<-5.00	<-5.00	70-90
	10 ^b	28.5 \pm 0.5	-6.54 \pm 0.24	<-5.00	<-5.00	<-5.00	<-5.00	40-60

^a Range: 10^{-4} – 10^{-2} M for nos. 1–6; 10^{-5} – 10^{-2} M for nos. 7–10. ^b Data are mean value \pm SD for a minimum of six electrodes.

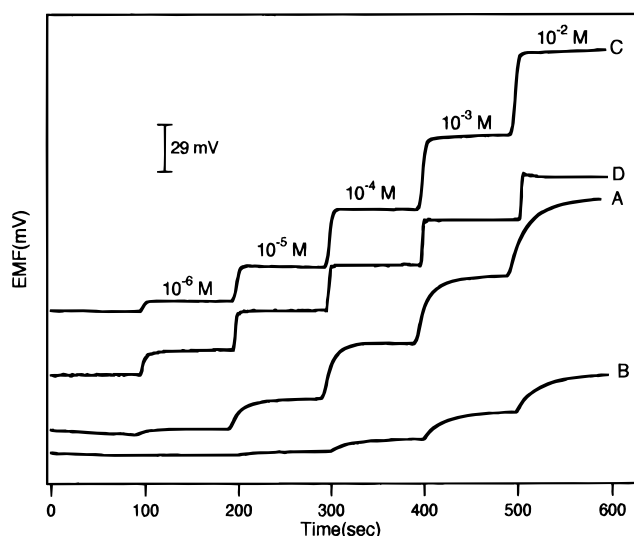


Figure 2. Dynamic response curves for SR membrane-based electrodes to the changes in concentration from 10^{-6} to 10^{-2} M $CaCl_2$ (background electrolyte, 0.05 M Tris-HCl buffer, pH 7.2). Curves: (A) membrane no. 1, (B) 2, (C) 5, and (D) 9.

exhibit poorly reproducible, nonlinear, and over-Nernstian responses to the change in pCa values, suggesting that the charged associates of the ionophore and monovalent calcium complex ions are part of the permeating species in those membranes.⁴⁴ On the other hand, the response of the type I membrane (membrane 3) prepared with a weaker calcium-complexing ligand, ETH 1001, was sub-Nernstian (18 mV/pCa).⁴⁰

Table 2 shows that DOA or DOS plasticized type II membranes have substantially lower bulk resistance compared to that of the type I membranes. Plasticizers added to the SR matrix also helped bring about uniform dissolution of ionophores in the membrane. It was noticed that the calcium-selective neutral carriers, especially ETH 129, doped in pure SR tend to crystallize out of the membrane during the curing period. On the other hand, the SR membranes with about 20 wt % plasticizers remain relatively transparent, without any crystals on their surfaces, for an extended period of time. However, the membranes prepared with higher weight percentages of plasticizers than those listed in Table 1 exhibited oily surfaces, owing to their limited solubility in the SR matrix. The dynamic response curve C in Figure 2 further demonstrates the advantage of adding plasticizer to the SR matrix: response

times are considerably shortened with type II membranes (e.g., $t(\Delta E/\Delta t)$ for membrane 5 is about 12 s).

As can be seen from Table 2, the SR matrix tends to degrade the calcium selectivities of the neutral carriers ETH 129 and ETH 1001. Although their calcium selectivities could be improved by varying the anionic site concentrations in the membrane,⁴¹ such optimization procedures are not easy to follow for the SR-based membranes, because the solubility of a common lipophilic additive, such as KTpCIPB, is limited, even in the plasticized SR matrix. Thus, we searched for a rather uncommon lipophilic additive for SR-based membranes to further reduce their resistance and to enhance their calcium selectivity.

Originally, the lipophilic salt TDATpCIPB (ETH 500) has been introduced to lower the high electrical resistance of microelectrode membranes without altering their selectivity.³¹ To our surprise, however, it was observed that the addition of 0.3 wt % ETH 500 to type II membranes not only lowered their bulk membrane resistance (see Table 2) but also corrected the problem of abnormal potentiometric response (compare curves C and D in Figure 2) while drastically improving their calcium selectivity. It was presumed that the dissociated cationic part of ETH 500, i.e., tetradodecylammonium, may play the role of trapped cation in the membrane after being replaced by the more lipophilic Ca^{2+} complexes of the neutral carrier, reducing the interference from monovalent ions or their carrier complex ions.³¹ Recognizable anionic interference at a high calcium concentration above 10^{-2} M may be taken as partial evidence for this hypothesis (type II membranes usually exhibit over-Nernstian response in that concentration range). When the measurements were made with $Ca(SCN)_2$ salt instead of $CaCl_2$, the type III membranes doped with the stronger calcium-binding ligand (ETH 129) suffered to a larger extent from interference by the lipophilic thiocyanate than those with ETH 1001.⁴⁴ Small amounts of additional KTpCIPB slightly alleviated such anionic interferences.

In Figure 3, the influence of sodium, the most abundant cation in clinical samples, on the potentiometric responses of ETH 129- and ETH 1001-doped PVC and type III membrane electrodes is compared. From these calibration plots, it can be seen that the

(41) Eugster, R.; Gehrig, P. M.; Morf, W. E.; Spichiger, U. E.; Simon, W. *Anal. Chem.* **1991**, *63*, 2285–2289.

(42) Miyahara, Y.; Simon, W. *Electroanalysis* **1991**, *3*, 287–292.

(43) Fogt, E. J.; Untereker, D. F.; Norenberg, M. S.; Meyerhoff, M. E. *Anal. Chem.* **1985**, *57*, 1998–2002.

(44) Morf, W. E. *The Principle of Ion-Selective Electrodes and of Membrane Transport*; Elsevier Scientific Publishing Co.: Amsterdam, 1981; Chapter 12.

(40) Bakker, E.; Willer, M.; Lerchi, M.; Seiler, K.; Pretsch, E. *Anal. Chem.* **1994**, *66*, 516–521.

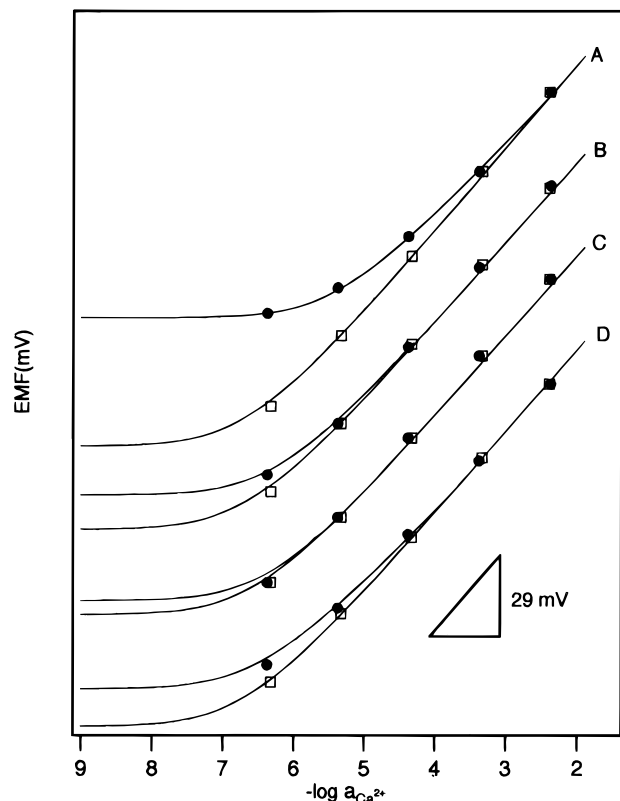


Figure 3. Response of calcium-selective electrodes to Ca^{2+} in the absence (\square) and presence (\bullet) of 100 mM Na^+ in 0.05 M Tris-HCl buffer, pH 7.2. ETH 1001-based (A) PVC membrane and (B) SR membrane 10; ETH 129-based (C) PVC membrane and (D) SR membrane 9.

type III and PVC-based membranes containing the same neutral carrier exhibit nearly identical response to calcium in the absence of interfering ions. In the presence of 100 mM sodium, however, the ETH 1001-doped type III membrane (membrane 10) exhibits clearly improved calcium selectivity compared to that of the corresponding PVC-based membrane; their respective logarithmic fixed-interference selectivity coefficients are -4.3 and -3.6 . For membranes containing ETH 129 (calibration curves D and C), both type III and PVC-based membranes exhibit similar calcium selectivity over sodium; their respective logarithmic fixed-interference selectivity coefficients are -4.3 and -4.6 . Type III membranes did not exhibit any significant response to H^+ , especially in the clinically relevant pH range (6.5 – 9.5).³³

All-Solid-State Calcium-Selective Electrodes. The response curves in Figure 4 demonstrate that the planar-type CWE sensor prepared with ETH 1001-doped type III membrane behaves like the corresponding conventional ISE. Type III membranes coated on metal electrodes usually required at least 2 days of curing time to give a stable potentiometric signal. Type III membrane-based CWEs cured for an extended period exhibited much less drift in their response potential and required no preconditioning of the membranes before the actual measurement. This result indicates that the potentiometric properties of SR-based membranes and the stability of membrane/metal interface are greatly dependent on the extent of their vulcanization.

Our recent study showed that addition of plasticizer to the RTV-1-type SR matrix does not significantly deteriorate its adhesive property, and even a highly plasticized SR membrane retains adhesion much more strongly than the PVC membrane.²⁰ Strong

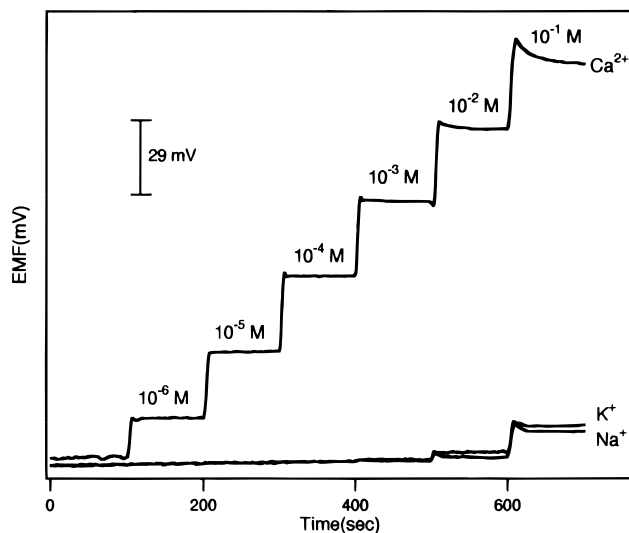


Figure 4. Dynamic response curves for the all-solid-state electrode coated with the SR membrane 10 to the changes in concentrations of Ca^{2+} , Na^+ , and K^+ from 10^{-6} to 10^{-1} M.

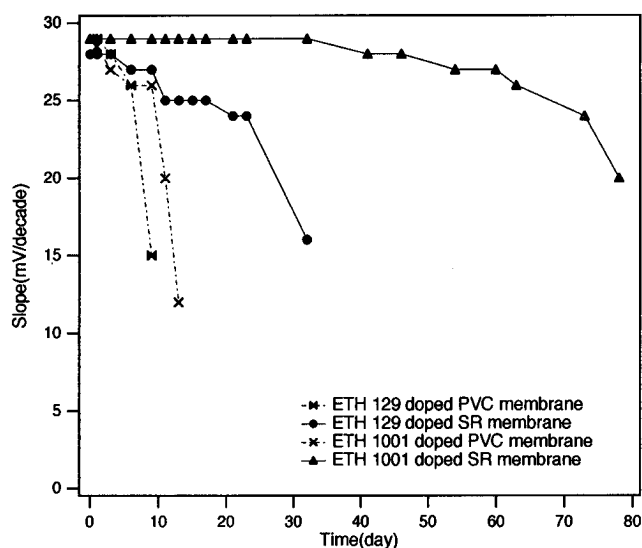


Figure 5. Variation of response slopes over time for CWEs based on ETH 129- and ETH 1001-doped PVC membranes and SR membranes 9 and 10. CWEs were kept in magnetically stirred deionized water throughout the measurement.

adhesion of the type III membranes to the inner solid contact substantially improved the lifetime of CWE sensors. Figure 5 shows the change in response slopes measured in the 10^{-5} – 10^{-2} M range for PVC- and type III membrane-based CWEs over time; when the electrodes were kept in magnetically stirred deionized water, slopes for the PVC-based CWEs were reduced to 20 mV/pCa from its initial value, 28 mV/pCa, in a week, while those for the type III membrane-based CWEs were still over 25 mV/pCa, even after several weeks. The type III membranes containing ETH 1001 exhibited 3 times longer lifetime, about 9 weeks, compared to those based on ETH 129.

It is commonly observed that polymer membrane-based all-solid-state ion sensors suffer from a large increase in noise level and potential drift over time due, in part, to osmotic transport of water into the thermodynamically ill-defined membrane/solid interface.^{42,43} Cha et al. found that such problematic potential variations could be reduced to a practically manageable level by improving the membrane adhesion.¹³ When several newly pre-

pared type III membrane-based CWEs were placed in a 10^{-3} M Ca^{2+} solution, their average potential drift in the first 24 h was only 2–3 mV, and no significant increase in noise level was observed near the end of their lifetime. CWEs based on these RTV-1-type calcium-selective membranes have potentiometric properties truly comparable to those of the corresponding conventional ISEs. Not only are the type III membranes easily applied to any all-solid-state electrodes using the screen printing method or a microdispensing system, but the sensors prepared with those membranes also exhibit highly reproducible sensor-to-sensor potentiometric performance.

ACKNOWLEDGMENT

This research was supported by the Ministry of Education, Korea, through the Basic Science Research Institute Program (BSRI-95-3405).

Received for review August 8, 1995. Accepted November 28, 1995.[⊗]

AC950789+

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1996.