

Silicone Rubber Blended with Polyurethane as the Matrix for Ion-Selective Membrane Electrodes

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(Received October 16, 1995)

Abstract : Silicone rubber-based sodium-selective membranes are developed for solid-state ion sensors. It was shown that the potentiometric performance of SR-based membranes are greatly dependent on the type of neutral carriers employed; among the three ionophores, *N,N,N',N'*-tetracyclohexyl-1,2-phenylenedioxydiacetamide (ETH 2120), bis[(12-crown-4)methyl]dodecylmethylmalonate (D12C4DMM) and monensin methyl ester (MME), examined, only ETH 2120 was compatible with the SR-based matrix. Addition of about 20 wt % plasticizer to the SR-based matrix provided the resulting membranes with potentiometric properties essentially equivalent to those of the corresponding PVC-based membranes. Owing to the strong adhesive strength of SR-based membranes, the CWEs coated with those membranes exhibited long lifetime with conventional electrode-like performance. Blending of PU into the SR matrix increased the lifetime of CWEs from two weeks to one month.

Keyword : ion-selective electrode, solid-state electrode, coated wire electrode (CWE), ISFET, silicone rubber matrix, polyurethane matrix, sodium-selective electrode

1. Introduction

In recent years, the desire to develop miniaturized and mass producible solid-state ion sensors, i.e., coated

wire-type electrodes (CWEs) and ion-selective field effect transistors (ISFETs), has been growing [1]. Plasticized PVC membranes containing small amounts of various electroactive components (e.g., ionophores

and lipophilic additives) have been the most commonly used ion-selective membranes for those solid-state type devices [2]. These membranes are directly cast on the sensing sites of the sensor without internal reference solution. However, the use of CWEs or ISFETs modified with PVC-based membranes has not been widespread yet because of a large drift in their potentiometric response and short lifetime [2]. It has been suggested that water molecules creep through the membrane and form thermodynamically ill-defined hydrated layer at the membrane/solid interface. Dissolved carbon dioxide may also permeate through the membrane and form carbonic acid at the interface with the hydrated layer, being the cause of the drift [3]. PVC-based membranes also have inherently weak adhesion to most solid surfaces and are eventually peeled off from the solid-state electrodes. Although these problems have often been dealt with separately, formation of ill-defined hydrated layer at the interface may result from the poor adhesive strength of the PVC-based membrane: for example, Cha et. al. found that the lifetime and potential stability of a solid-state ion sensor are greatly improved by employing alternate polymer matrices with increased adhesive strength [4, 6].

Several methods have been proposed to attach the ion-sensing membrane layer to the surface of solid-state devices; physical fastening of the membrane, modification of PVC to enhance the interaction with the hydroxyl group bearing surface, chemical grafting of the sensing layer either by thermal or photochemical curing methods, and use of alternate polymers (e.g., Urush, epoxy resin, poly(methyl acrylate), polyurethane and silicone rubber, etc.) [4 - 22]. However, these methods are often too complicated to apply or result in poor electrochemical performance. Thus, a design of solvent polymeric ion sensing membranes that are easily mountable on any solid-state device without

compromising their potentiometric performance is prerequisite in developing microfabricated ion-selective sensor arrays for various applications.

van der Wal et. al. have shown that an ISFET modified with the valinomycin-doped room temperature vulcanizing-type silicone rubber (3140 RTV SR) membrane exhibit potentiometric response characteristics comparable to those of the corresponding PVC-based membranes with improved lifetime [20]. It was also found in our laboratory that addition of 10 - 20 wt % of plasticizer (bis(2-ethylhexyl)adipate) into the same membrane elongated its lifetime to more than 200 days. However, sodium- and calcium-selective neutral carriers doped in non-plasticized SR membrane exhibited either very slow or negligible potentiometric responses. It was presumed that the poor signal to noise ratio results from the high resistance of SR-based membranes [23, 24]. Also there are substantial evidence that SR-based membranes form a resistive film on their surface, resulting in slow ion exchange kinetics at the surface. The use of polyurethane matrix to prepare ISEs was suggested more than two decades ago [26]. However, its actual use has been realized recently by Cha et. al. and by Lindner et. al. [4, 5]. They found that an aliphatic polyurethane (Tecoflex)-based membranes perform like the corresponding PVC-based membranes on a solid-state ion sensor with much improved adhesion and biocompatibility. Furthermore, Tecoflex PU matrix is compatible with most neutral carriers incorporated and has much lower electrical resistance than that of the SR matrix.

It seems reasonable to presume that the ion sensing membranes prepared with the blend of SR and PU matrix would complement the drawbacks of each polymer. In this contribution, the electrochemical performance of the ion-selective membranes prepared with the SR/PU matrix has been investigated, focusing on the

development of sodium-selective CWEs.

2. Experimental

Reagents

3140 RTV silicone rubber (SR) was a product of Dow Corning Co. (Midland, MI, USA), while poly(vinyl chloride) (PVC), *N,N,N',N'*-tetracyclohexyl-1,2-phenylenedioxydiacetamide (ETH 2120), bis[(12-crown-4)methyl]dodecylmethylmalonate (D12C4DMM), bis(2-ethylhexyl)adipate (DOA), bis(2-butylpentyl) adipate (BBPA), *o*-nitrophenyl *n*-octyl ether (NPOE), and potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB) were purchased from Fluka Chemie AG (Buch, Switzerland). Monensin methyl ester (MME) was a product of Calbiochem-Novabiochem (La Jolla, CA). Tecoflex polyurethane (SG-80A) was purchased from Thermedics (Woburn, MA). Tris(hydroxymethyl)amino methane was obtained from Sigma Chemical Co. (St. Louis, MO, USA). All other chemicals used were analytical-reagent grade. Standard solutions and buffers were prepared with deionized water (18 Mohm.cm).

Preparation of Ion-Selective Membranes

PVC-based calcium-selective membranes were prepared by incorporating sodium ionophores into the plasticized PVC matrices; their compositions have been optimized as described in the literature. Their typical compositions are 33 wt % PVC, 66 wt % NPOE, BBPA or DOS, 1 wt % ionophore. Various 3140 RTV SR-based membranes were prepared by dissolving 198 mg of silicone rubber, 2 mg of sodium-selective neutral carrier (ETH 2120, sodium ionophore VI or Monensin methyl ester), and varying amounts of plasticizer (0 - 90 μ l of DOA or DOS) and lipophilic additives (0 - 0.54 mg of KTpClPB) in 0.4 ml THF. For SR/PU-based membranes, 2 parts of Tecoflex PU was blended with 8

parts of SR; their exact compositions in weight percents are given in Table I. All membrane cocktails were cast in glass ring placed on teflon plates for conventional ion-selective electrodes or directly deposited on planar-type silver electrodes. PVC membrane cocktails were dried at room temperature for at least 24 hours, while those based on 3140 RTV SR for 2 - 4 days.

Table 1. Composition of various sodium-selective membranes in wt %.

Type	Matrix			ionophore ^a	plasticizer
	PVC	SR	PU		
A	33.0			1.0	66.0 ^b
B		99.0		1.0	
C		77.7		0.8	21.5 ^c
D		79.0	19.8	1.2	
E		59.1	14.8	0.9	25.2 ^c

^a MME, D12C4DMM or ETH 2120; ^b NPOE for MME and D12C4DMM, and DOA for ETH 2120;

^c DOA for all ionophores

EMF measurements

Initial evaluation for 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, Zurich, Switzerland). For all electrodes, 0.1 M NaCl 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). 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 (K^+ , and Na^+) stepwise from 10^{-6} to 10^{-1} M, and the measurements of emf values were taken every second at room temperature. Selectivity coefficients were determined by the separate solution-matched potential method. Both SR- and SR/PU-based sodium-selective membranes optimized in the conventional electrode were applied on the silver electrodes (modified CWEs; area, 0.8 mm^2) and they were dipped into the cocktail solution 5 times. In order to see the sensor-to-sensor reproducibility, several CWEs were prepared from the same cocktail solution for each set of experiment. These electrodes were dried in the atmosphere for 2 to 4 days. All electrochemical evaluation for these CWEs was performed by the same experimental methods as described for conventional electrodes.

3. Results and Discussion

Figure 1 (a) shows the dynamic response characteristics of the D12C4DMM-doped membranes measured with the conventional electrodes. It was found that the D12C4DMM ionophore is not compatible with non-plasticized SR and SR/PU matrices. On the other hand, addition of about 20 wt % of DOA plasticizer to the matrix dramatically improved their potentiometric properties to a better degree than those of the PVC-based membranes. Potentiometric characteristics of plasticized SR and SR/PU-based membranes are summarized in Table 2 along with those of the corresponding PVC-based membrane. It seems that the electrochemical properties of the ionophores may have been altered by their chemically active surrounding, where the polycondensation reaction of the SR matrix proceeds upon exposure to the atmosphere [6]. In general, except for the valinomycin-doped membranes

[20], most neutral carriers do not behave properly in the SR or SR/PU matrix. Figure 1 (b) shows the dynamic response of the type E membrane coated on a CWE. Although the type D membrane exhibited virtually the same response characteristics in the conventional electrode, it had shorter lifetime on the CWE than the type E membrane.

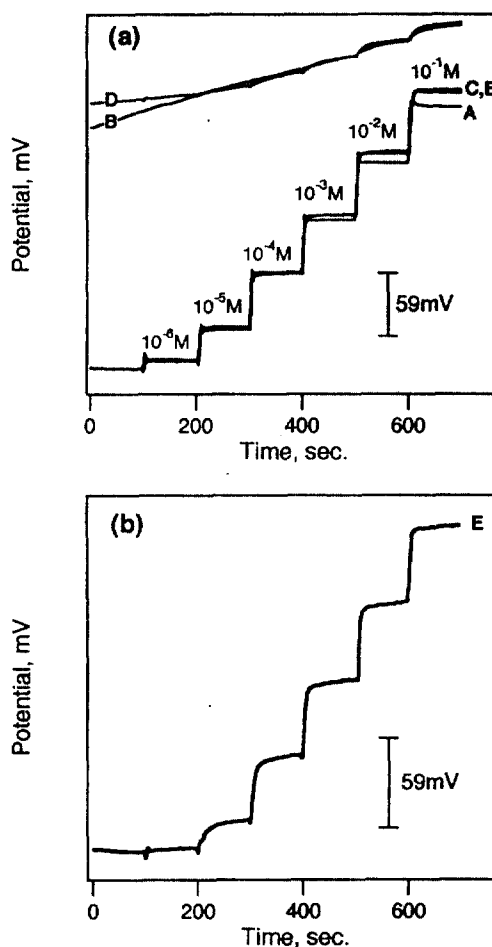


Figure 1. (a) Dynamic response curves for various D12C4DMM-doped membranes obtained with the conventional electrode. Compositions of the membranes are given in Table 1.; (b) Response of the Type E membrane coated on a silver electrode.

Although there was certain improvements in their responses in the non-plasticized membranes, the potentiometric behavior of MME-doped membranes were similar to that of D14C2DMM-doped membranes. However, the detection limits for the SR- and SR/PU-based membranes were increased by an order of magnitude compared to that for the PVC-based membranes. These results are summarized in Figure 1 (a). Furthermore, the response slope and detection limit for CWEs with MME-doped SR/PU membranes became much worse than those of the corresponding conventional electrode, indicating that MME is not a suitable neutral carrier for the SR-based membranes.

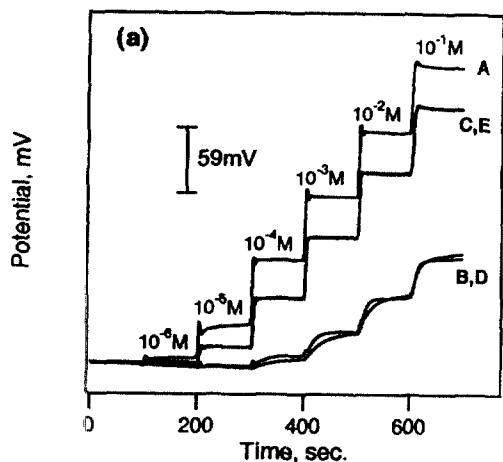


Figure 2. (a) Dynamic response curves for various MME-doped membranes obtained with the conventional electrode.

Unlike the other two sodium-selective ionophores, D12C4DMM and MME, the ETH 2120 ligand exhibit substantial electrochemical activity in the non-plasticized SR (Type B)- and SR/PU (Type D)-based membranes; their response slopes were 47.8 and 53.3 mV/dec, respectively. It is noticeable that the blending of

PU (Type D) enhances the response slope, reflecting the increased compatibility of ETH 2120 ligand with the SR matrix. As can be seen from Figure 3 (a), however, addition of plasticizer was necessary to further improve the response slopes and the response times comparable to those of PVC-based membranes. These results strongly suggest that plasticizers incorporated in polymer matrix not only provide a liquid-like structure

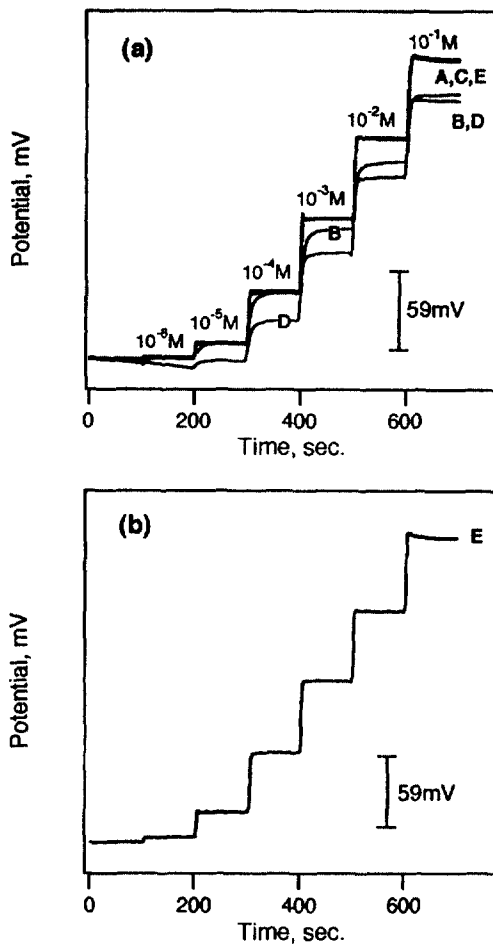


Figure 3. (a) Dynamic response curves for various ETH 2120-doped membranes obtained with the conventional electrode.; (b) Response of the Type E membrane coated on a silver electrode.

Table 2. Potentiometric characteristics of D14C2DMM-doped membranes

Type	Slope (mV/dec)	Detection limit (log a_{Na^+})	Selectivity Coefficient ($\log K_{\text{Na},j}^{\text{pot}}$)				
			K ⁺	Li ⁺	NH ₄ ⁺	Ca ²⁺	Mg ²⁺
A	50.8	-5.69	-2.02	-3.04	-2.41	-3.04	-3.88
C	55.9	-5.53	-1.76	-2.98	-2.34	-3.33	-4.17
E	54.8	-5.58	-1.79	-3.02	-2.29	-3.35	-4.20

Table 3. Potentiometric characteristics of ETH 2120-doped membranes

Type	Slope (mV/dec)	Detection limit (log a_{Na^+})	Selectivity Coefficient ($\log K_{\text{Na},j}^{\text{pot}}$)				
			K ⁺	Li ⁺	NH ₄ ⁺	Ca ²⁺	Mg ²⁺
A	55.2	-4.89	-1.84	-1.21	-0.36	-1.84	-4.91
B	47.8	-5.01					
C	56.2	-4.87	-1.53	-1.12	-0.60	-2.20	-4.09
D	53.3	-4.53					
E	56.2	-4.86	-1.50	-1.14	-0.71	-2.17	-4.54

to the ion-selective membranes, but also enhance the ion-exchange kinetics by removing the resistive film formed at the membrane surface. Although SR and PU are in a rubbery state at usual working temperature, ionophores in those matrices may not have sufficient transmembrane mobility without the aid of an appropriate plasticizer. However, the content of plasticizer added to these matrices could be reduced to less than 20 wt %, which is substantially lower than the amount, 66 wt %, required for the common PVC-based membranes. The overall performance of the ETH 2120-doped membranes are summarized in Table 2.

Figure 3 (b) shows the characteristic dynamic response of the silver electrode coated with the Type E membrane; while the CWE with the Type C membrane exhibit similar response, it has shorter lifetime (~ 2

weeks) than the one with the Type E membrane (~ 1 month).

4. Conclusion

SR-based sodium-selective membranes have been developed for solid-state electrodes. It has been shown that the performance of SR-based membranes is greatly dependent on the type of ionophore incorporated; among the three commercial sodium-selective ionophores tested in this study, only ETH 2120 was compatible with the SR or SR/PU matrix. Addition of about 20 wt % of plasticizer to SR-based matrix drastically improved their potentiometric properties. Application of plasticized SR-based membranes on the silver electrodes results in CWEs whose properties are comparable to those of

conventional electrodes. Although the initial response behavior of SR and SR/PU-based membranes were almost identical, the later exhibited longer lifetime on the CWE.

Acknowledgment

This research was supported by the Korea Science and Engineering Foundation (94-0800-07-01-3).

References

1. R. K. Meruva, E. Malinowska, R. W. Hower, R. B. Brown and M. E. Meyerhoff, *Transducer 95-Eurosensor IX*, 855 (1995).
2. Y. Myahara and W. Simon, *Electroanalysis*, **3**, 287 (1991).
3. E. J. Fogt, D. F. Untereker, M. S. Norenberg and M. E. Myerhoff, *Anal. Chem.*, **57**, 1998 (1985).
4. G. S. Cha, D. Liu, M. E. Meyerhoff, H. C. Cantor, A. R. Midgley, H. D. Goldberg and R. B. Brown, *Anal. Chem.*, **63**, 1666 (1991).
5. E. Lindner, V. V. Cosofret, S. Ufer, R. P. Buck, W. J. Kao, M. R. Neuman and J. M. Anderson, *J. Biomed. Mater. Res.*, **28**, 591 (1994).
6. B. K. Oh, C. Y. Kim, H. J. Lee, K. L. Rho, G. S. Cha and H. Nam, *Anal. Chem.*, [in press].
7. T. Satchwill and D. J. Harrison, *Electroanal. Chem.* **202**, 75 (1986).
8. G. J. Moody, J. D. R. Thomas and J. M. Slater, *Analyst*, **113**, 1703 (1988).
9. V. V. Cosofret, M. Erdoesy, R. P. Buck, W. J. Kao, J. M. Anderson, E. Lindner and M. R. Neuman, *Analyst* **119**, 2283 (1994).
10. G. Blackburn and J. J. Janata, *Electrochem. Soc.* **129**, 2580 (1982).
11. M. Battilotti, R. Colilli, I. Giannini and M. Giongo, *Sens. Actuators* **17**, 209 (1989).
12. N. Jaffrezic-Renault, J. M. Chovelon, H. Perrot, P. LePerchec and Y. Chevalier, *Sens. Actuators B* **5**, 67 (1991).
13. E. J. R. Sudholter, P. D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld and D. N. Reinhoudt, *Sens. Actuators* **17**, 189 (1989).
14. E. J. R. Sudholter, P. D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld and D. N. Reinhoudt, *Anal. Chim. Acta* **230**, 59 (1990).
15. J. A. J. Brunink, R. J. W. Lugtenberg, Z. Brozka, J. F. J. Engebensen and D. N. Reinhoudt, *J. Electroanal. Chem.* **378**, 185 (1994).
16. S.-I. Wakida, M. Yamane, K. Higashi, K. Hihiro and Y. Ujihara, *Sens. Actuators B* **B1(1-6)**, 412. (1990).
17. S. Johnson, G. J. Moody and J. D. R. Thomas, *Anal. Proc.* **27**, 79 (1990).
18. G. S. Cha and R. B. Brown, *Sens. Actuators B1*, 281 (1990).
19. L. Cunningham and H. Freiser, *Anal. Chim. Acta* **180**, 271 (1986).
20. P. D. van der Wal, M. Skowronska-ptasinska, A. van den Berg, P. Bergveld, E. J. R. Sudholter and D. N. Reinhoudt, *Anal. Chim. Acta* **231**, 41 (1990).
21. (a) K. Kimura, T. Mutsuba, Y. Tsujimura and M. Yokoyama, *Anal. Chem.* **64**, 2508 (1992).
(b) Y. Tsujimura, M. Yokoyama and K. Kimura, *Anal. Chem.* **67**, 2401 (1995).
22. J. H. Shin, D. S. Sakong, H. Nam and G. S. Cha, *Anal. Chem.* [in press].
23. P. D. van der Wal, E. J. R. Sudholter, B. A. Boukamp, H. J. M. Bouwmeester and D. N. Reinhoudt, *J. Electroanal. Chem.* **317**, 153

- (1991).
24. E. Lindner, Z. Niegriesz, K. Toth, E. Pongor, T. R. Berube and R. P. Buck *J. Electroanal. Chem.* **259**, 67 (1989).
26. U. Fiedler and J. Ruzicka, *Anal. Chim. Acta*, **67**, 179 (1973).