

Solvent-Processible Polymer Membrane-Based Liquid Junction-Free Reference Electrode

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A new type of liquid junction-free reference electrode system is devised by employing solvent-processible polymer membranes. The membranes are formulated with either a one-component silicone rubber or an aromatic-type polyurethane as the matrixes. The optimized formulations incorporate both cation- and anion-exchange sites (i.e., potassium tetrakis(*p*-chlorophenyl)borate and tridodecylmethylammonium chloride) and, in the case of silicone rubber, a plasticizer. The silicone rubber-based membrane, while possessing minimal response toward most ions, is found to display a near-Nernstian response to pH change. The aromatic polyurethane matrix formulation, however, is not sensitive to pH over a wide range (i.e., pH 2–12) and is shown to exhibit only a small emf variation (within ± 2 mV) toward a wide variety of salts added even at very high concentrations (i.e., up to 0.1 M). Potentiometric emf responses of ISEs (e.g., Na^+ , K^+ , Ca^{2+} , Cl^-), whether paired with a polymer membrane-based reference electrode or with a conventional liquid junction-type reference electrode, are shown to be remarkably similar within the precision of the measurement setup. The feasibility of adapting the proposed reference electrode to the planar solid-state sensor format is also demonstrated.

There is a growing interest in the development of alternatives to the conventional liquid junction-type reference electrode, particularly for use in miniature ion sensor systems. To this end, various technically challenging methods have been proposed to introduce an ion-insensitive structure on a base transducer.^{1–14} One approach involves covering a metallic surface (i.e., Ag/AgCl)

with an electrolyte-doped polymeric material (e.g., poly(vinyl acetate)/KCl,¹ quaternized poly(chloromethylstyrene)/Cl[–],² Reflex (a KCl-doped vinyl ester resin),³ poly(vinyl chloride) (PVC)/NaCl,⁴ etc.). In another approach, the reference signal was generated from two separate anion- and cation-conducting membranes coated on Ag/AgCl electrodes connected in parallel.⁵ These membranes consisted of PVC, a plasticizer (bis(2-ethylhexyl) sebacate), a lipophilic salt, and a cation- or an anion-exchange material, respectively (i.e., potassium tetrakis(*p*-chlorophenyl)borate (K-TpCIPB) and a copolymer of methacrylic acid and methyl methacrylate in the cation-exchange membrane and tridodecylmethylammonium chloride (TDMA-Cl) and poly[*N*-(4-vinylbenzyl)-*N,N*-dimethylamine] in the anion-exchange membrane). With respect to ion-sensitive field effect transistor (ISFET) applications, various types of reference field effect transistors (REFETs) have been fabricated by introducing a pH- or an ion-insensitive surface on the ISFET gate: e.g., coating hydrophobic, insulating, and ion-blocked films (Parylene, Teflon, polystyrene) by vacuum deposition, ion beam sputtering, and plasma polymerization,^{6–9} chemically grafting an aliphatic chain (alkyl- or chloroalkylsilane),^{10–12} covalently anchoring an ion-unblocking polymeric membrane (polyacrylate or polybutadiene) formed by photopolymerization,¹³ coating a bilayer film consisting of an electropolymerized inner layer and a photopolymerized outer layer,¹⁴ etc. With a differential arrangement consisting of an ISFET and a REFET, the conventional reference electrode can be replaced by a metal electrode, which is not required to exhibit a stable potential.^{10,13}

In this contribution, we propose a new approach of fabricating potentiometric reference electrodes employing polymeric membranes. Researchers engaged in developing solvent polymeric membrane-type ion-selective electrodes (ISEs) have had a frustrating experience identifying membranes insensitive toward most ionic species. However, if such a membrane is systematically developed and characterized, it may serve as a reference electrode that does not require a salt bridge. The Ag/AgCl-type reference electrodes are by far the most commonly used in flow-through ISE measurements (e.g., in automated clinical analyzers such as Stat Profile/NOVA biomedical, GEM Premier/Instrumentation Laboratory, etc.). Such arrangements require the use of two flow channels that are merged downstream to form a liquid junction:

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Table 1. Compositions of Membranes Tested in This Study^a

membrane no.	matrix					lipophilic additive				plasticizer DOA ^j
	3140RTV ^b	PU ^c 20	PU40	PVC ^d	Teco-PU ^e	ETH 500 ^f	TDMA-Cl ^g	K-TpCIPB ^h	TPAP-Cl ⁱ	
1	77.6									22.4
2	76.9					0.9				22.2
3	77.2						0.5			22.3
4	76.8							0.4	0.6	22.2
5	76.9						0.5	0.4		22.2
6		100								
7			100							
8			98.9			1.1				
9			98.9					0.5	0.6	
10			98.9				0.6	0.5		
11				33.3						66.7
12					96.8		1.7	1.5		

^a In wt %. ^b Silicone rubber. ^c Aromatic polyurethane. ^d High-molecular-weight poly(vinyl chloride). ^e Tecoflex polyurethane. ^f Tetradodecylammonium tetrakis(*p*-chlorophenyl)borate. ^g Tridodecylmethylammonium chloride. ^h Potassium tetrakis(*p*-chlorophenyl)borate. ⁱ Tetrakis[tris(dimethylamino)phosphoranylideneamino]phosphonium chloride. ^j Bis(2-ethylhexyl) adipate.

the first is the sample channel that directs the sample over the ISEs, and the second is the reference channel that directs a reference fluid across the Ag/AgCl electrode. This is because the Ag/AgCl electrode responds to various chemical species including chloride. However, the liquid junction-free reference electrode proposed in the present work could be placed adjacent to the ISEs within the sample channel, making it possible to eliminate the use of an additional reference channel.

Solvent-processible polymer-based reference electrodes are easy to fabricate and miniaturize, and membranes may be deposited on a solid substrate through the dispensing or the screen printing method. Therefore, the proposed reference system is well adapted to the fabrication of planar-type solid-state sensor devices. In this work, various reference electrode membranes are formulated from each of the silicone rubber and polyurethane materials that we have investigated previously as the ion-selective membrane matrixes.^{15–21} The characteristics of these membranes are examined as mounted in conventional electrode bodies or on planar solid-state electrodes. In particular, the degree of the electrode response is evaluated toward most physiologically important ionic species (e.g., Na⁺, K⁺, Ca²⁺, Cl[−], salicylate, etc.). Potentiometric ion responses of several ISEs paired with a polymer membrane-based reference electrode are compared to those obtained with a conventional liquid junction-type reference electrode. Finally, the analytical utility and limitations of the proposed reference system are discussed based upon the findings of this work.

EXPERIMENTAL SECTION

Reagents. The sources of reagents used were as follows: high-molecular-weight PVC, bis(2-ethylhexyl) adipate (DOA), K-TpCIPB, TDMA-Cl, tetradodecylammonium tetrakis(*p*-chlorophenyl)borate (ETH 500), tetrakis[tris(dimethylamino)phosphoranylideneamino]phosphonium chloride (TPAP-Cl), sodium ionophore III (ETH 2120), calcium ionophore I (ETH 1001), and 1,4-butanediol (BD) from Fluka (Buch, Switzerland); valinomycin from Sigma (St. Louis, MO); 4,4'-methylenebis(phenyl isocyanate) (MDI) from Kanto (Tokyo, Japan); poly(tetramethylene ether glycol) (PTMEG) of 2000 molecular weight from Aldrich (Milwaukee, WI); Tecoflex SG-80A polyurethane from Thermedics (Woburn, MA); and 3140 RTV silicone rubber from Dow Corning (Midland, MI). All other chemicals used were analytical-reagent grade. Standard solutions and buffers were prepared with deionized water.

Synthesis of Aromatic Polyurethanes. A series of aromatic polyurethanes were synthesized as described in our earlier work:²¹ i.e., prepolymerization of a long-chain diol (PTMEG) with an excess of aromatic diisocyanate (MDI), chain extension of the prepolymer with a short-chain diol (BD), and finally capping of unreacted isocyanates with absolute methanol. The molar ratio between MDI and total diols was adjusted to 1:1. The weight percentage of soft segments was equal to that of PTMEG. These polyurethanes were denoted as PU $_{nn}$ (e.g., PU20, PU40, PU60, and PU80), where nn indicates the weight percentage of soft segment contents in the synthesized polyurethanes.²¹

Preparation of Polymer Membranes. Reference electrode membranes were prepared by dissolving 3140 RTV silicone rubber in THF or aromatic polyurethanes in DMF, along with given amounts of other active membrane components, and then casting the cocktails in a glass ring placed on a flat plate, as described in our previous articles (see refs 15–20 (silicone rubber) and 21 (polyurethane) for details). In the present work, aromatic polyurethane membranes, which were formulated with PU20 or PU40, were cured in an oven at 55 °C for at least 12 h, while those based upon the silicone rubber were dried for 3–5 days at room temperature. Table 1 summarizes the compositions of the reference electrode membranes examined in this study. Sodium-

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potassium-, and calcium-selective membranes were prepared by incorporating ETH 2120, valinomycin, and ETH 1001, respectively, into PVC matrixes as described elsewhere.^{16–19,22}

Evaluation of Polymer Membranes. The potentiometric behaviors of reference electrode membranes were evaluated in the conventional ISE configuration as described elsewhere.^{16–21} Small disks (5.5 mm) were punched from cast films and mounted in Philips electrode bodies (IS-561; Glasbläserei Möller, Zürich, Switzerland) containing 0.1 M KCl as an internal filling solution. The potential changes of the polymer membrane-based reference electrodes were measured against a conventional liquid junction-type reference electrode (Orion model 90-02; sleeve-type double-junction Ag/AgCl electrode), using an IBM AT-type computer equipped with a custom high-impedance input 16-channel analog-to-digital converter. Dynamic response curves were obtained through the addition of standard solutions to a background electrolyte (0.05 M tris(hydroxymethyl)aminomethane (Tris)-H₂SO₄, pH 7.4) at room temperature.

The potentiometric responses of sodium, potassium, calcium, and chloride ISEs obtained with a membrane-based reference electrode were compared to those with the Orion double-junction reference electrode. PVC-based sodium, potassium, and calcium ISEs were prepared by employing the Philips electrode bodies: the internal filling solutions were 0.1 M NaCl, KCl, and CaCl₂, respectively. An Ag/AgCl wire was used as a chloride ISE. In this experiment, standard solutions were added stepwise to an artificial serum solution which does not contain ionic species under test (the basic composition: 8 mM NaH₂PO₄/1.5 mM Na₂HPO₄/2.0 mM CaCl₂/0.8 mM MgCl₂/4.5 mM KCl/0.05 mM NH₄Cl/4.7 mM glucose/2.5 mM urea). The emf differences between the ISEs and the reference electrode were measured at room temperature using the aforementioned 16-channel potentiometric setup. The response of electrodes to pH changes was tested by adding aliquots of LiOH to a solution of 11.4 mM boric acid/6.7 mM citric acid/10.0 mM NaH₂PO₄ at room temperature. The solutions were magnetically stirred during the recording of all emf values.

Solid-State Sensors. Planar-type solid-state electrodes with multiple sites were fabricated by printing silver electrodes on aluminum oxide, as described previously.^{16,18,19} As a preliminary application, a PVC/valinomycin-based potassium-selective site and a polyurethane matrix reference site were formed on a single chip. A small volume of membrane cocktail solution, typically 5 μ L, was applied on the silver electrode contacts and the surrounding dielectric layer with a pneumatic dispenser (EFD model 1000XL; Providence, RI). These sensors were dried in ambient air for 12 h and tested in the same manner as their Philips-body counterparts, as described in the previous section.

RESULTS AND DISCUSSION

Initially, we examined four different classes of solvent-processible polymeric materials as matrixes for use in fabricating reference electrode membranes: i.e., PVC, silicone rubber, aliphatic Tecoflex, and aromatic polyurethanes. While providing excellent electrochemical performances as ISE matrixes, PVC was found to be an inadequate material for the preparation of a hardly responsive membrane. PVC requires the use of a plasticizer to

lower its resistance to an acceptable level, but such a plasticized membrane, even without containing an ionophore or a lipophilic ionic additive, usually exhibits a sizable response particularly toward lipophilic anions (e.g., perchlorate, salicylate, etc.). Tecoflex aliphatic polyurethane is one of the most successful alternatives to PVC as the ISE matrixes.^{23–27} However, membranes employing this material were found to induce a greater anionic response than other matrix-based membranes. Thus, in this study, we focused on formulating hardly responsive membranes with 3140 RTV silicone rubber and aromatic-type polyurethane matrixes.

Another motivation of selecting the RTV silicone rubber in formulating a reference electrode membrane is its highly adhesive characteristic toward a wide range of substrates. In fabricating planar-type sensors (e.g., solid-state sensors), adhesion of the membranes to the sensor surface is typically a determining factor for sensor lifetime and stability.^{19,23} However, the electrical resistance of the 3140 RTV matrix employed in this study is very high, as is typical of silicone rubber membranes. Incorporation of the ionophore to the matrix would decrease the membrane resistance, but this approach is not desired in the case of formulating an ion-insensitive reference electrode membrane. Instead in this work, a plasticizer was used to reduce the signal noise associated with the high resistance of the RTV membranes, as demonstrated in our previous work.^{15–20} It was also shown that the addition of plasticizer to the silicone rubber matrix does not significantly deteriorate its adhesive property, and even a highly plasticized RTV membrane retains adhesion much more strongly than the PVC membrane. Table 1 lists five different compositions (membranes no. 1–5) employing such a plasticized silicone rubber matrix. Lipophilic ionic additives were examined in an attempt to further lower the membrane resistance and to balance the cationic and anionic responses of the membranes.

Figure 1 illustrates effects of employing different ionic additives on the response behaviors of the plasticized RTV membranes toward added salts. The plain plasticized RTV membrane (1), prepared even without adding an ionic additive, exhibited a rather large ion response toward added salts, although less than those of plasticized PVC matrix membranes (not shown). The cationic response toward KCl, NaCl, or CaCl₂, as shown in Figure 1, may be due to the presence of anionic sites (e.g., silanol groups or ionizable impurities) within the RTV membrane phase. On the other hand, an anionic response observed toward added sodium salicylate can be attributed to the fact that the selectivity of the solvent polymeric-type membrane is affected by the relative solubility of the individual ion in the membrane phase, more lipophilic ions being preferred: i.e., the membrane response is greater toward salicylate than toward sodium. The use of an additive consisting of both lipophilic cations and anions (i.e., ETH 500), while reducing the signal noise (not clearly shown), did not induce an observable change in the response pattern of the

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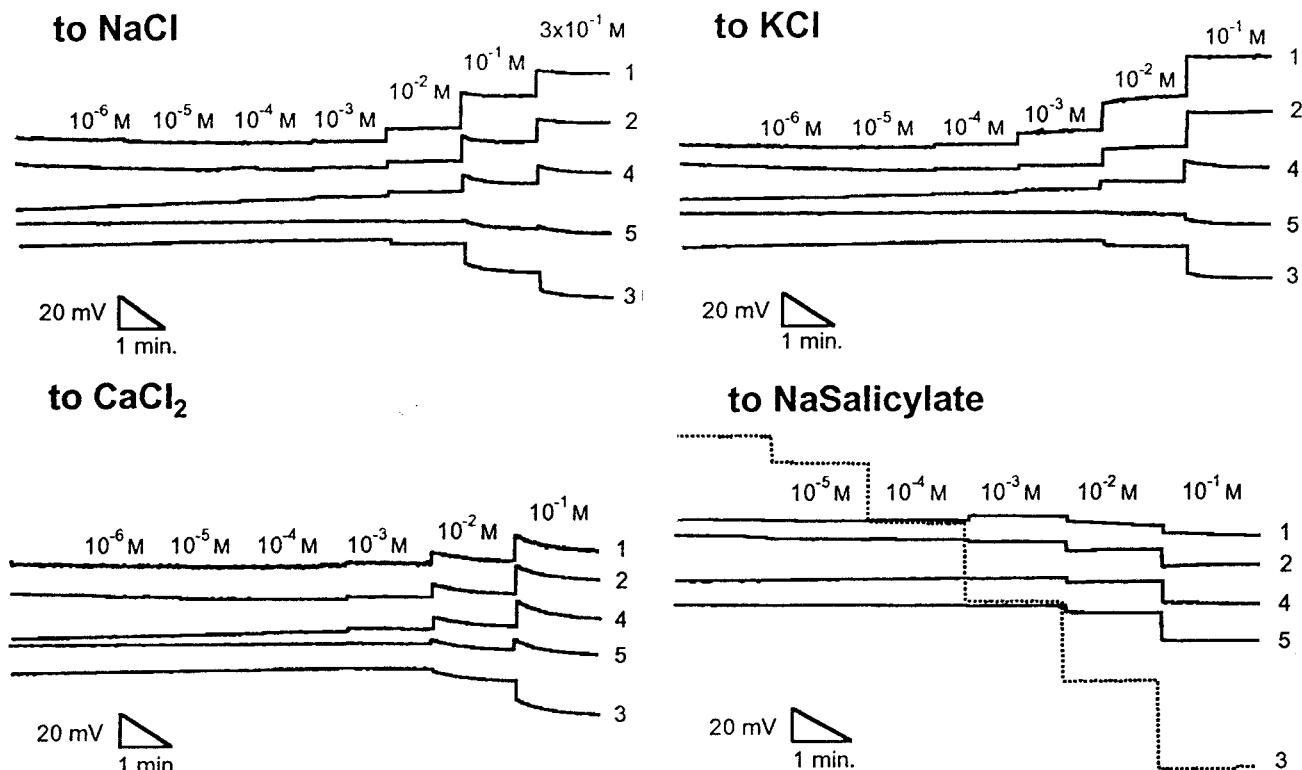


Figure 1. Dynamic emf response of silicone rubber-based membranes toward varying amounts of salts added in a buffer: (1) 3140 RTV/DOA, (2) 3140 RTV/DOA/ETH 500, (3) 3140 RTV/DOA/TDMA-Cl, (4) 3140 RTV/DOA/K-TpCIPB/TPAP-Cl, and (5) 3140 RTV/DOA/K-TpCIPB/TDMA-Cl (membranes 1–5 in Table 1).

plasticized RTV membrane (membrane 2 compared to membrane 1 in Figure 1). This is because the addition of ETH 500 increases only the total amounts of ionic sites with the same number for the cationic and the anionic sites. As expected, a membrane incorporating an anion-exchanger-type additive (i.e., TDMA-Cl) (membrane 3) exhibited an increased response toward anionic species. Consequently, the membrane's ability to detect cationic and anionic species was balanced by varying the amounts of both a cation exchanger (i.e., K-TpCIPB) and an anion exchanger (i.e., TDMA-Cl or TPAP-Cl). Membranes 4 (K-TpCIPB/TPAP-Cl) and 5 (K-TpCIPB/TDMA-Cl) exemplify the compositions optimized by such an approach. In the case of the K-TpCIPB/TDMA-Cl-based membrane (5), the emf signals were negligible toward added salts at concentrations lower than 0.1 M for KCl and NaCl, 0.01 M for CaCl_2 , or 0.001 M for sodium salicylate. This type of membrane can act as a pseudoreference electrode only for a diluted sample system (e.g., blood samples diluted more than 10 times with a buffer).

Polyurethane is a block copolymer which consists of soft and hard segments. Polyurethanes from different commercial sources indeed have widely different chemical and physical properties, depending on the types and relative compositions of their building blocks, typically isocyanates and polyols. Having low glass transition temperatures, polyurethanes may be used to prepare ISE membranes with no or a reduced amount of plasticizer. We have previously synthesized a series of MDI-based aromatic polyurethanes with different contents of soft segments (i.e., 20–80 wt % of PTMEG) and investigated the effect of varying matrix properties on their electrochemical behavior.²¹ In this work, polyurethanes with 60–80 wt % soft segments (i.e., PU60 and

PU80) were shown to yield ISE membranes that exhibit significant potentiometric responses in the absence of plasticizer and/or lipophilic additive. On the other hand, membranes with lower levels of soft segments (e.g., PU40) did not show appreciable emf responses in the absence of plasticizer, even with the addition of a cation exchanger (K-TpCIPB) up to 50 mol % (refer to Figure 5 in ref 21). On the basis of these observations, PU20 and PU40 were selected as the matrixes in formulating reference electrode membranes for the present study.

Five different compositions (membranes 6–10) employing aromatic polyurethanes are listed in Table 1, and their response behaviors toward different salts are shown in Figure 2. Surprisingly, all of the membranes employing PU20 and PU40, regardless of using lipophilic ionic additives, did not exhibit appreciable emf signals toward relatively high concentrations (up to 0.01 M) for all of the added salts. These results, along with the previous observation that the response of ionophore-doped polyurethane membranes drastically decreases with increasing content of hard segments,²¹ may imply that the hard segments greatly reduce the solubility and mobility of ions in the membrane phase and hinder the formation or diffusion of ion–ionophore complexes. This may render the PU20 or PU40 matrix membranes ion-insensitive in the absence of plasticizer. Compared to the PU20, the PU40 has an enhanced solvent processibility due to an increased level of low-melting, flexible soft segments and, thus, is preferred as the membrane matrix. The resistance of polyurethane membranes prepared with lipophilic ionic additives (membranes 8–10) was lower than those without additives (membrane 7) by a factor of 20–100 and comparable to those of typical PVC-based ISE membranes. In the subsequent experiments, we selected the

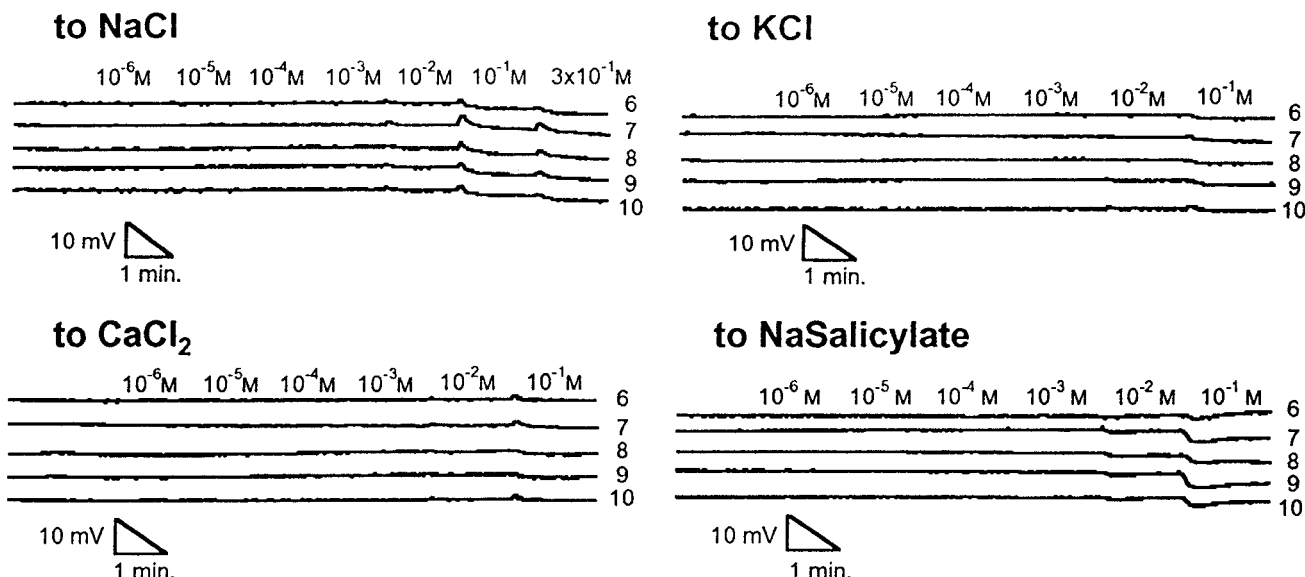


Figure 2. Dynamic emf response of aromatic polyurethane-based membranes toward varying amounts of salts added in a buffer: (6) PU20, (7) PU40, (8) PU40/ETH 500, (9) PU40/K-TpCIPB/TPAP-Cl, and (10) PU40/K-TpCIPB/TDMA-Cl (membranes 6–10 in Table 1).

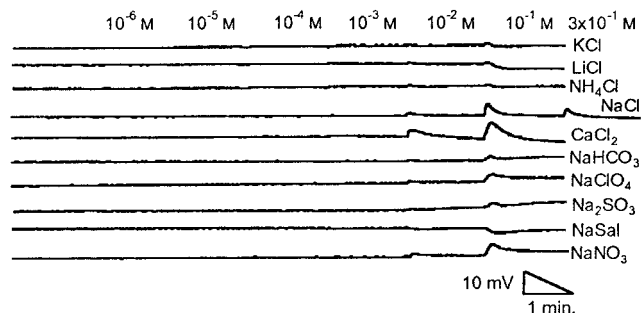


Figure 3. Dynamic emf response of the aromatic polyurethane (PU40)-based membrane toward varying amounts of salts added in a buffer (membrane 10 in Table 1).

composition employing PU40, TDMA-Cl, and K-TpCIPB (i.e., membrane 10 in Table 1) to further examine the characteristics of the polyurethane-based reference electrode membranes.

In Figure 3, the ion-insensitive characteristic of the PU40 matrix membrane is further demonstrated. As can be seen, its response behavior is similar toward a wide variety of added salts, and the emf signals are indeed negligible except for showing small variations at 0.1 M concentrations: after reaching equilibrium, the observed potential changes were within ± 2 mV. The pH sensitivity of the aromatic PU40 matrix membrane was also examined and compared with those of three different types of polymer membranes as shown in Figure 4 (see Table 1 for detailed membrane compositions). A near-Nernstian response behavior (i.e., a slope of 56 mV per unit pH change in the range of pH 2–10) displayed by the RTV-based membrane (5) may be attributed to the presence of silanol groups within the polymer membrane structure: the 3140 RTV employed is a silanol-terminated poly(dimethylsiloxane). In the case of the PVC matrix membrane (11), the pH response (a slope of 38 mV per unit pH change) seems to be induced by the plasticizer incorporated. On the other hand, the pH sensitivity of the Tecoflex polyurethane membrane (12) at alkaline pHs (a slope of 42 mV per unit pH change) appears to originate from nitrogens or oxygens of aliphatic urethane units. However, the pH sensitivity was not

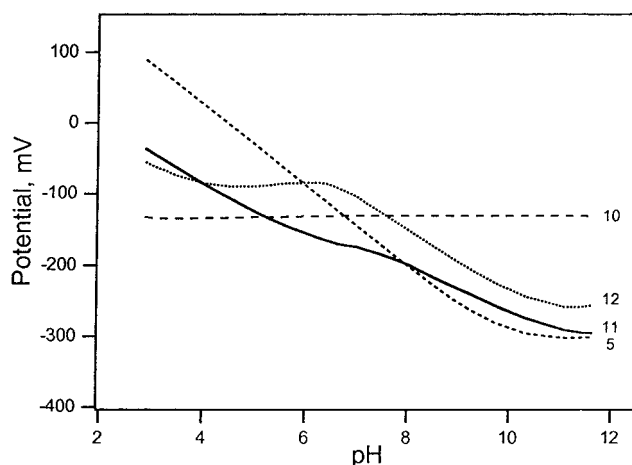


Figure 4. pH response of polymer membranes employing different matrices: (5) 3140 RTV/DOA/TDMA-Cl/K-TpCIPB, (10) PU40/TDMA-Cl/K-TpCIPB, (11) PVC/plasticizer, and (12) Tecoflex/TDMA-Cl/K-TpCIPB (membranes 5 and 10–12 in Table 1).

observed when the aromatic-type polyurethane matrix (10) was used. This may be explained by a decreased basicity of the aromatic urethane nitrogens: i.e., the lone-pair electron of the nitrogen or oxygen is further delocalized with the adjacent phenyl group. With the aromatic PU40 matrix membrane, an appreciable emf response was not detected over a wide pH region (i.e., standard deviation $s = 1.5$ mV; estimated for the entire range of pH 2–12). Such a pH-insensitive membrane is desired for use as the reference electrode membrane.

The analytical utility of the proposed aromatic polyurethane-based ion-insensitive membrane system was examined in an artificial serum by using it as a reference electrode to construct dynamic calibration plots of four different ISEs (Na^+ , K^+ , Ca^{2+} , Cl^-) in the range of clinical interest (curve a in Figure 5). For comparison purpose, another set of calibration plots was simultaneously obtained by using a commercial Orion liquid junction-type reference electrode (curve b in Figure 5). The individual dynamic response behavior of each ISE paired with the polymer

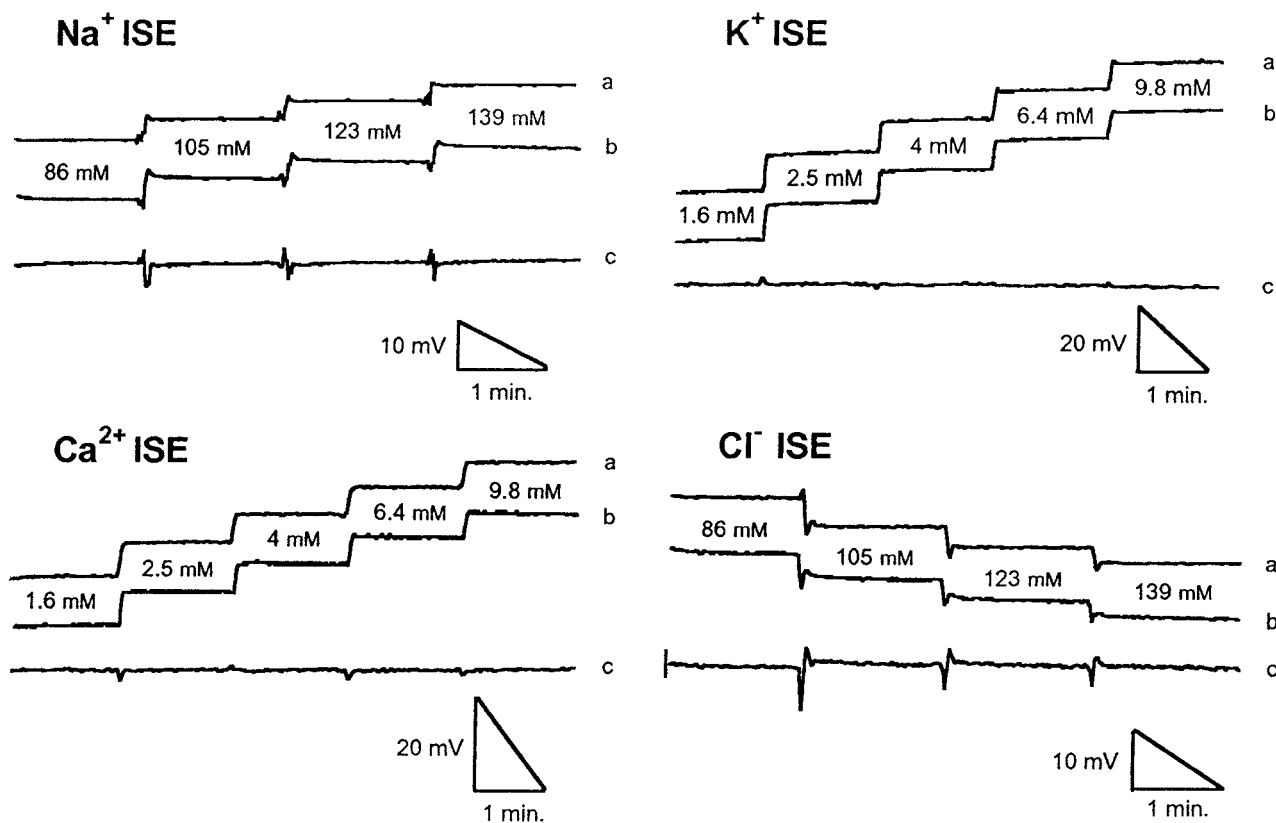


Figure 5. Dynamic calibration plots of four different ISEs in artificial serum, as coupled with the aromatic PU40 membrane (10)-based reference electrode (curve a) and with the Orion liquid junction-type reference electrode (curve b); and normalized difference plots between the PU40 and Orion reference electrode systems (curve c).

membrane-type reference electrode was virtually the same as that obtained with the Orion liquid junction reference electrode, as can be clearly seen from the normalized difference plots (curve c in Figure 5) between the polymer membrane and the Orion reference electrode systems: standard deviations of the difference plots, estimated with equilibrium potentials over the entire range tested, were less than 0.5 mV in all cases. The slopes of the ISEs were also estimated, and differences in values obtained for each of the two reference electrodes were within the precision of our potentiometric measurement setup: slope (mV/decade) 51.6 (PU40), 51.3 (Orion) for Na⁺ ISE; 55.9 (PU40), 55.7 (Orion) for K⁺ ISE; 31.7 (PU40), 31.5 (Orion) for Ca²⁺ ISE; and -49.6 (PU40), -49.3 (Orion) for Cl⁻ ISE.

In the solid-state planar sensor format, the ion-selective membrane is directly connected to the planar metal contact, having no internal electrolyte solution. This direct contact is usually accomplished by dispensing (or screen-printing) the membrane cocktail solution directly on top of the metal contact. The proposed aromatic polyurethane-based formulation is solvent-processible, and thus, can be easily adapted to the solid-state sensor format. Furthermore, the aromatic polyurethane membranes develop good adhesion to sensor surfaces, as is typical of polyurethane matrixes. In this preliminary work, a valinomycin-based potassium-selective PVC membrane and an aromatic PU40-based reference electrode membrane were deposited on a planar sensor chip with multiple electrode sites, as described in the Experimental Section. In Figure 6, the dynamic calibration plot of this miniature combination sensor (curve a) is compared with that obtained simultaneously by connecting the potassium-sensing

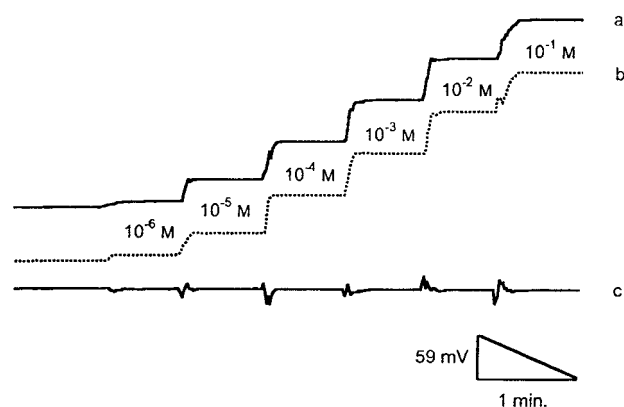


Figure 6. Dynamic calibration plots of the solid-state potassium sensor paired with the polymer-based solid-state reference electrode (curve a) and with the Orion reference electrode (curve b); and a normalized difference plot between the polymer and Orion reference electrode systems (curve c).

site to the Orion reference macroelectrode (curve b), and the difference plot between these two measurements is constructed (curve c, $s = 0.2$ mV). As can be seen, the response behaviors of two different combinations were remarkably similar with virtually the same slope of 57.2 mV/decade for 10⁻⁵–10⁻¹ M potassium. The ion response of the solid-state potassium combination sensor was not significantly altered after 1 week of use.

In this report, we have described a new type of liquid junction-free reference electrode employing solvent-processible polymer matrixes. The silicone rubber-based formulation, while possessing

minimal response toward most ions, displayed a near-Nernstian response to pH change and thus can find a limited use as a reference electrode (e.g., for samples diluted with a buffer). Particularly exciting is the performance of the aromatic polyurethane matrix formulation: it exhibits only a small emf variation even at very high salt concentrations and no appreciable response over a wide pH range. Given that the process for making a reference electrode on top of the planar solid-state sensor is compatible with that for ion-selective membranes, it is likely that the proposed approach will offer a relatively simple method to

mass fabricate various types of miniature combination sensor devices.

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