

Potentiometric Properties of Ion-Selective Electrode Membranes Based on Segmented Polyether Urethane Matrices

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Potentiometric responses of polyurethane (PU)-based membranes containing valinomycin and varying amounts of plasticizer (DOA) and/or lipophilic additive (KTpCIPB) were examined as a function of soft segment [poly-(tetramethylene ether glycol)] contents in aromatic diisocyanate-based PU matrices. Upon increasing the weight percentages (w_{soft}) of soft segments, which in part behave like a built-in plasticizer, providing the matrices with rubbery structure (glass transition temperature below -58°C), the amounts of DOA and/or KTpCIPB necessary to result in near-Nernstian response (e.g., slope $> 50\text{ mV/decade}$) to potassium were substantially lowered. The apparent effect of adding plasticizer to PU-based membranes was comparable to that resulting from an increase of free carrier concentration in normal PVC-based membranes. Owing to the chemical interaction between mobile anionic sites and urethane chains, plasticizer-free PU membranes could be prepared with the PU matrices with high soft segment contents ($w_{\text{soft}} \geq 60\text{ wt } \%$). PUs composed of $60 \leq w_{\text{soft}} < 80\text{ wt } \%$ were recommended as the matrix for fabricating ISE membranes with no or low plasticizer content.

Ion and biosensors based on solvent polymeric membranes, typically the highly plasticized poly(vinyl chloride) (PVC) doped with small amounts of electroactive components (e.g., ionophore and/or lipophilic ionic salt), are now routinely utilized in the field of biomedical analysis.^{1–4} PVC-based sensing membranes, however, suffer from several drawbacks that limit their lifetime and applicability;^{5–10} these include the dissolution of membrane components into the biological fluids, weak adhesion of the

membrane to solid-state sensor devices, and adsorption of biological components that leads to thrombus formation on the membrane surface. Many researchers have attempted to solve such problems by employing alternate polymer matrices (e.g., PVC derivatives,^{11–15} silicone rubber,^{16–19} polyurethane,^{20–26} etc.).

Among the many polymer matrices besides PVC, polyurethanes (PUs) attract particular interest, especially in the biomedical applications involving all-solid-state or miniaturized in vivo ion sensors.^{10,21–26} Some polyurethanes such as Tecoflex and Pellethane are useful materials not only for manufacturing implantable medical devices but also for formulating ISE membranes,^{20,26,27} they yield transparent, physically durable, adhesive, and chemically stable sensing membranes with electrochemical properties comparable to those of PVC-based membranes. Furthermore, having low glass transition temperatures, PU-based ISE membranes may be prepared with no or a reduced amount of plasticizer, which is often the cause of blood clotting, rejection responses, and tissue inflammation.^{23,24}

Although a few studies have demonstrated the utility of PU-based membranes in biomedical applications, there is little

- (1) (a) Wang, J. *Anal. Chem.* **1993**, *65*, 450R–453R; (b) **1995**, *67*, 487R–492R.
- (2) Yim, H. S.; Kibbey, C. E.; Ma, S.-C.; Kliza, D. M.; Liu, D.; Park, S.-B.; Torre, C. E.; Meyerhoff, M. E. *Biosens. Bioelectron.* **1993**, *8*, 1–38.
- (3) Collison, M. E.; Meyerhoff, M. E. *Anal. Chem.* **1990**, *62*, 425A–434A.
- (4) Oesch, U.; Ammann, D.; Simon, W. *Clin. Chem.* **1986**, *32*, 1448–1459.
- (5) Davies, M. L.; Hamilton, C. J.; Murphy, S. M.; Tighe, B. J. *Biomaterials* **1992**, *13*, 971–978.
- (6) Armstrong, R. D.; Horvai, G. *Electrochim. Acta* **1990**, *35*, 1–7.
- (7) Dinten, O.; Spichiger, U. E.; Chaniotakis, N.; Gehrig, P.; Rusterholz, B.; Morf, W. E. *Anal. Chem.* **1991**, *63*, 596–603.
- (8) Oesch, U.; Simon, W. *Anal. Chem.* **1980**, *52*, 692–700.
- (9) Dürselen, L. F. J.; Wegmann, D.; May, K.; Oesch, U.; Simon, W. *Anal. Chem.* **1988**, *60*, 1455–1458.
- (10) Meyerhoff, M. E. *Trends Anal. Chem.* **1993**, *12*, 257–266.

- (11) Satchwill, T.; Harrison, D. J. *J. Electroanal. Chem.* **1986**, *202*, 75–81.
- (12) Moody, G. J.; Thomas, J. D. R. *Analyst* **1988**, *113*, 1703–1707.
- (13) Cosofret, V. V.; Erdösy, M.; Buck, R. P.; Kao, W. J.; Anderson, J. M.; Lindner, E.; Neuman, M. R. *Analyst* **1994**, *119*, 2283–2292.
- (14) Lindner, E.; Cosofret, V. V.; Nahir, T. M.; Buck, R. P. *ACS Symp. Ser.* **1994**, *556*, 149–157.
- (15) Ma, S. C.; Chaniotakis, N. A.; Meyerhoff, M. E. *Anal. Chem.* **1988**, *60*, 2293–2299.
- (16) van der Wal, P. D.; Skowronska-Ptasinska, M.; van den Berg, A.; Bergveld, P.; Sudhölter, E. J. R.; Reinhoudt, D. N. *Anal. Chim. Acta* **1990**, *231*, 41–52.
- (17) Malinowska, E.; Oklejas, V.; Hower, R. W.; Brown, R. B.; Meyerhoff, M. E. *Transducer 95-EuroSensor IX* **1995**, 851–854.
- (18) Shin, J. H.; Sakong, D. S.; Nam, H.; Cha, G. S. *Anal. Chem.* **1996**, *68*, 221–225.
- (19) Oh, B. K.; Kim, C. Y.; Lee, H. J.; Rho, K. L.; Cha, G. S.; Nam, H. *Anal. Chem.* **1996**, *68*, 503–508.
- (20) Fiedler, U.; Ruzicka, J. *Anal. Chim. Acta* **1973**, *67*, 179–193.
- (21) 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.
- (22) Liu, D.; Meyerhoff, M. E. *Anal. Chim. Acta* **1993**, *274*, 37–46.
- (23) Lindner, E.; Cosofret, V. V.; Ufer, S.; Buck, R. P.; Kao, W. J.; Neuman, M. R.; Anderson, J. M. *J. Biomed. Mater. Res.* **1994**, *28*, 591–601.
- (24) Espadas-Torre, C.; Meyerhoff, M. E. *Anal. Chem.* **1995**, *67*, 3108–3114.
- (25) Bratov, A.; Abramova, N.; Muñoz, J.; Domínguez, C.; Alegret, S.; Bartoli, J. *Anal. Chem.* **1995**, *67*, 3589–3595.
- (26) Cosofret, V. V.; Erdösy, M.; Raleigh, J. S.; Johnson, T. A.; Neuman, M. R.; Buck, R. P. *Talanta* **1996**, *43*, 143–151.
- (27) Coury, A. J.; Slaikeu, P. C.; Calahan, P. T.; Stokes, K. B.; Hobot, C. M. *J. Biomater. Appl.* **1988**, *3*, 130–179.

information relating their potentiometric performance to the physical and chemical nature of PU matrices.^{20,26} The lack of such studies may be traced to the difficulties in finding PUs with appropriate physical and electrochemical properties; PUs from different commercial origins have widely different characteristics (e.g., phase transition temperature, mechanical properties, adhesive strength, electrical resistance, solubility, etc.), depending on the types and relative compositions of their building blocks, typically isocyanates and polyols.^{27,28}

Considering the recently renewed interest in PU-based sensing membranes, it is desired that a fundamental study that accounts for the effect of varying matrix properties on their electrochemical behavior be available.^{29,30} To this end, a series of 4,4'-methylenbis(phenyl isocyanate) (MDI)-based PUs with different contents of soft segments (20–80 wt %) [poly(tetramethylene ether glycol), PTMEG] was synthesized by altering their relative stoichiometric ratios.^{28,31} Potassium-selective membranes based on valinomycin were prepared with these PU matrices. In this contribution, by examining thermal, mechanical, and chemical properties of PU-based membranes and their potentiometric responses with respect to the contents of soft segments, plasticizer, and/or lipophilic additive, we attempted to correlate them with the operational characteristics of PU-based ISE membranes.

EXPERIMENTAL SECTION

Reagents. The sources of reagents used were as follows: selectophore grade valinomycin, bis(2-ethylhexyl) adipate (DOA), potassium tetrakis(*p*-chlorophenyl)borate (KTpCIPB), high molecular weight poly(vinyl chloride) (PVC), and 1,4-butanediol (BD) from Fluka (Buch, Switzerland); Tecoflex SG-80A from Thermedics Inc. (Woburn, MA); poly(tetramethylene ether glycol) (PTMEG) of 2000 molecular weight from Aldrich Chemical Co. (Milwaukee, WI); and 4,4'-methylenbis(phenyl isocyanate) (MDI) from Kanto Chemical Co. (Tokyo, Japan). All other solvents and chemicals employed in this study were of analytical-reagent grade. All solutions were prepared with deionized water (18 M Ω ·cm).

Preparation of Aromatic Polyurethanes. The synthesis of aromatic polyurethanes was performed in three steps, 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.³¹ 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. All reagents were carefully demoi-
 sturized before use.

A calculated amount of PTMEG with about 10 mL of DMF was introduced into the thermostated and dry nitrogen-flushed reaction vessel while the mixture was constantly stirred with an anchor-type mechanical stirrer. Subsequently, monomeric MDI was added to the homogenized PTMEG solution. The temperature of the reaction vessel was gradually increased to 60 °C for an hour while the vigorous exothermic prepolymerization process was taking place, and the vessel was maintained at the same temperature for an additional hour to complete the reaction. A short-chain diol, BD, was then added to the prepolymer in an ice

bath. The chain extension reaction was initially carried out at room temperature for an hour and further at 60 °C for 2–3 h. During the synthesis, a small amount of DMF was occasionally added to the reacting mixture to reduce its viscosity. Upon completing the polymerization, about 2 mL of absolute methanol was added to the product to cap the unreacted isocyanates.

Hereafter, these polyurethanes are denoted as PU $_{nn}$ (e.g., PU20, PU40, PU60, and PU80), where nn indicates the weight percentage of soft segment contents (w_{soft}) in the synthesized PU.

Preparation and Potentiometric Evaluation of Ion-Selective Membranes. Four types of potassium-selective membranes were prepared by incorporating 1 wt % valinomycin into the following compositions: four different PUs composed of 20, 40, 60, and 80 wt % soft segments (type 1); type 1 PUs plasticized with 22, 44, 66, and 77 wt % DOA (type 2); type 1 PUs with 10, 30, 50, 70, and 90 mol % KTpCIPB relative to the ionophore (type 3); and type 2 PUs with KTpCIPB (50–70 mol %) (type 4). The compositions of each membrane are listed in Table 1. The same type of Tecoflex PU-based membranes and PVC-based membranes with a conventional composition (33 wt % PVC, 66 wt % DOA, and 1 wt % valinomycin) were also prepared for comparison.

The membrane cocktails of PU20 were prepared by dissolving all components in DMF, PU40 in a mixed solvent of DMF and THF, and PU60 and PU80 in THF. These cocktail solutions were then poured into a glass ring (i.d. 22 mm) placed on a slide glass or Teflon plate and dried over a day at room temperature. Small disks were punched from the cast films and mounted in Philips electrode bodies (IS-561; Glasblaserei Möller, Zürich, Switzerland) containing 0.1 M KCl as internal filling solution. All electrodes were presoaked in deionized water over 24 h before the emf measurements.

In all cases, potentiometric evaluation of the electrodes was performed in a 0.05 M Tris-HCl buffer of pH 7.2 using a static arrangement.¹⁹ Selectivity coefficients with respect to potassium were calculated from response potentials measured in 0.1 M cation chloride solutions buffered with 0.05 M Tris-HCl (pH 7.2) using the separate solution-matched potential method (SSM II).³² Response times of electrodes were also estimated according to the IUPAC recommendation, taking the time interval from the instant of sample injection to the initial point where $\Delta E/\Delta t$ becomes less than 0.1 mV/min on the dynamic response curves (concentration step, $10^{-3} \rightarrow 10^{-2}$ M). It should be noted that the response times measured in this manner include the mixing time of injected sample with the background solution.

Characterization of Aromatic Polyurethanes. Molecular weights (MW) of the synthesized polyurethanes were estimated using gel permeation chromatography (GPC; Shimadzu LC-6AD) with polystyrene standards (Aldrich Chemical Co.; MW from 20 000 to 200 000). Phase transition temperatures of polyurethanes as well as those of PU-based ion-selective membranes were measured using differential scanning calorimetry (DSC; Stanton Redcroft DSC 700). About 14 mg of PU placed in an aluminum sample cup was melted first at 240 °C for 2 min, and subsequently the melt was quenched at –150 °C to erase the previous thermal history. Measurements were made from –150 to 200 °C with a

(28) Dieterich, D.; Grigat, E.; Hahn, W. In *Polyurethane Handbook*; Oertel, G., Ed.; Hanser Publishers: Munich, 1985; Chapter 2.

(29) Moody, G. J.; Saad, B.; Thomas, J. D. R. *Analyst* **1987**, *112*, 1143–1147.

(30) Horvai, G.; Gráf, E.; Tóth, K.; Pungor, E.; Buck, R. P. *Anal. Chem.* **1986**, *58*, 2735–2740.

(31) Leung, L. M.; Koberstein, J. T. *Macromolecules* **1986**, *19*, 706–713.

(32) (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 $K_{A,B}^{\text{pot}}$ values. *Pure Appl. Chem.* **1995**, *67*, 507–518.

Table 1. Compositions and Electrochemical Properties of PU-Based Potassium-Selective Membranes

membrane type	no.	matrix	composition (wt %) [PU/Val/DOA/KTpCIPB (mol %)]	T_g (°C)	slope ^a (mV/decade)	det limit (-log [K ⁺])	$\log K_{K^+,j}^{POT}$	
							$j = Na^+$	$j = NH_4^+$
type 1	1	PU20	99/1/0/0	-58	nr			
	2	PU40	99/1/0/0	-62	nr			
	3	PU60	99/1/0/0	-67	nr			
	4	PU80	99/1/0/0	-74	34.2	4.6	-3.0	-1.8
type 2	5	PU20	77/1/22/0		nr			
	6		55/1/44/0		37.9	5.2	-3.9	-2.4
	7		33/1/66/0		55.0	5.4	-4.4	-2.2
	8	PU40	77/1/22/0	-85	6.8			
	9		55/1/44/0	-108	54.2	5.2	-4.0	-1.9
	10		33/1/66/0	-114	56.0	5.2	-5.0	-1.9
	11	PU60	77/1/22/0	-69	9.5			
	12		55/1/44/0	-81	53.5	5.8	-3.1	-2.0
	13		33/1/66/0	-98	53.1	5.7	-3.1	-2.0
	14		22/1/77/0	-99	54.2	5.6	-3.7	-2.0
	15	PU80	77/1/22/0		49.3	5.1	-3.7	-1.8
	16		55/1/44/0		54.6	5.6	-4.0	-1.9
	17		33/1/66/0		54.6	5.9	-4.4	-2.0
	18	PU20	99/1/0/10		nr			
	19	PU40	99/1/0/10	-63	nr			
	20		99/1/0/30	-65	nr			
	21		99/1/0/50	-66	nr			
type 3	22		99/1/0/70	-63	45.6	5.0	-3.4	-1.8
	23	PU60	99/1/0/10		33.8	4.6	-3.6	-1.8
	24		99/1/0/30		37.1	5.0	-3.1	-1.8
	25		99/1/0/50		40.6	4.9	-3.5	-1.8
	26		99/1/0/70		51.6	5.0	-3.6	-1.8
	27		99/1/0/90		51.7	4.9	-3.6	-1.9
	28	PU80	99/1/0/10		50.3	4.4	-3.1	-1.6
	29		99/1/0/30		53.4	4.8	-3.1	-1.6
	30		99/1/0/50		55.8	4.7	-3.3	-1.6
	31		99/1/0/70		55.2	4.6	-3.4	-1.6
	32		99/1/0/90		52.6	4.5	-3.2	-1.4
type 4	33	PU40	77/1/22/70		53.6	5.2	-3.8	-1.8
	34		55/1/44/70		55.2	5.3	-3.6	-1.8
	35		33/1/66/70		56.0	5.2	-3.6	-1.9
	36	PU60	77/1/22/70		54.6	5.4	-3.9	-2.0
	37		55/1/44/70		56.2	5.6	-4.0	-2.0
	38		33/1/66/70		56.2	5.6	-3.9	-2.0
	39	PU80	77/1/22/50		56.9	5.4	-3.8	-1.8
	40		55/1/44/50		57.1	5.6	-3.8	-1.8
	41		33/1/66/50		58.2	5.6	-3.5	-1.8

^a Range: 10^{-4} – 10^{-1} M; nr, negligible response.

heating rate of 25 °C/min under a flowing nitrogen atmosphere.³³ FT-IR spectra of PU membranes were obtained with thin PU60 films containing 0, 4, and 10 wt % KTpCIPB.

RESULTS AND DISCUSSION

The structure of aromatic PUs synthesized in this study, which is similar to that of Pellethane, is shown in Figure 1, along with that of aliphatic Tecoflex PU. The average molecular weights of aromatic PUs were between 98 000 and 118 000. As can be seen from the typical DSC thermogram of PU in Figure 2, PUs have two-phase domains, i.e., low-melting soft segments with flexible long-chain polyether units, and high-melting hard segments with stiff urethane units.³³ PU-based membranes thus exhibit varying physical and chemical properties, depending on their soft and hard segment compositions. For example, the membranes prepared with PU20 were brittle, opaque, and soluble in DMF; those from PU40 were hard, opaque, and partially soluble in THF; those from PU60 were elastic, transparent, and soluble in THF; and those from PU80 were malleable, transparent, and soluble in THF.

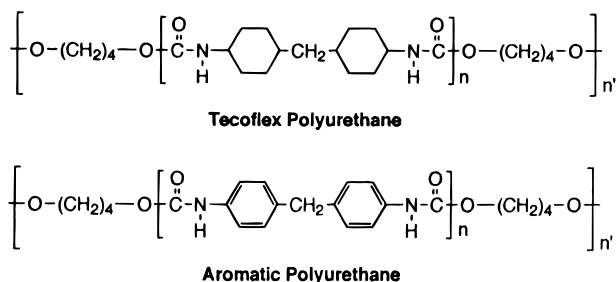


Figure 1. Structure of the aromatic polyurethane and aliphatic Tecoflex polyurethane.

Potentiometric properties of PU-based membranes also varied with the composition of PU matrix employed: the response curves in Figure 3 demonstrate that valinomycin-based PU membranes (type 1) containing 20–60 wt % soft segments exhibit negligible response to potassium, while that with 80 wt % is appreciable [34 mV/decade and $t(\Delta E/\Delta t) = 7.2$ s]. The same type of Tecoflex PU membrane behaved like an aromatic PU membrane with 60 < w_{soft} < 80 wt %.

While these results indicate that the soft segments in PU act in part as a built-in solvent for the neutral carrier doped in it, the

(33) van Bogart, J. W. C.; Bluemke, D. A.; Cooper, S. L. *Polymer* **1981**, 22, 1428–1438.

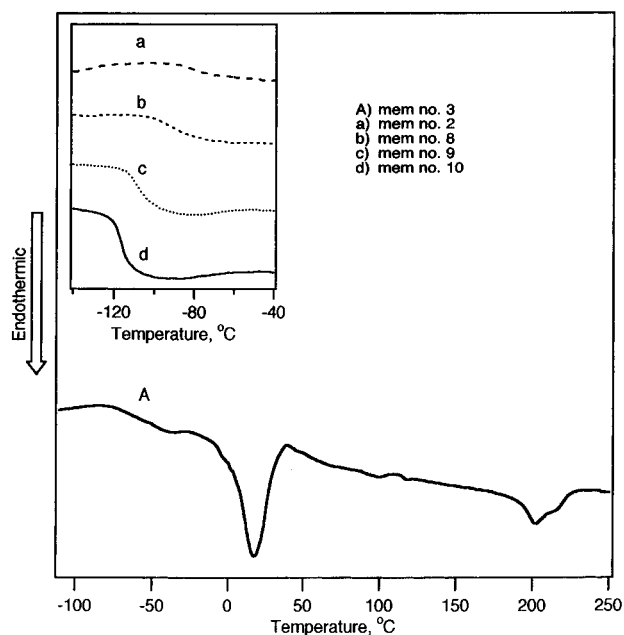


Figure 2. (A) DSC thermograms of pure PU60. Inset (a–d): Variation of the glass transition temperatures of PU40 with increasing plasticizer contents.

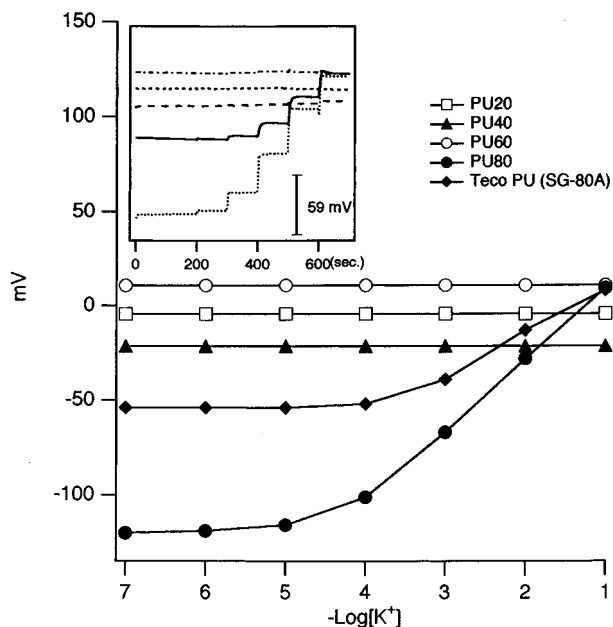


Figure 3. Potentiometric responses of type 1 membrane-based electrodes to potassium. Inset shows their dynamic responses [$t(\Delta E/\Delta t) \approx 7$ s].

potentiometric performance of type 1 membrane electrodes may be limited by the poor diffusion and/or dissolution of carrier molecules and their ion complexes within the membrane.^{34–39} It is also plausible that a high free energy barrier associated with

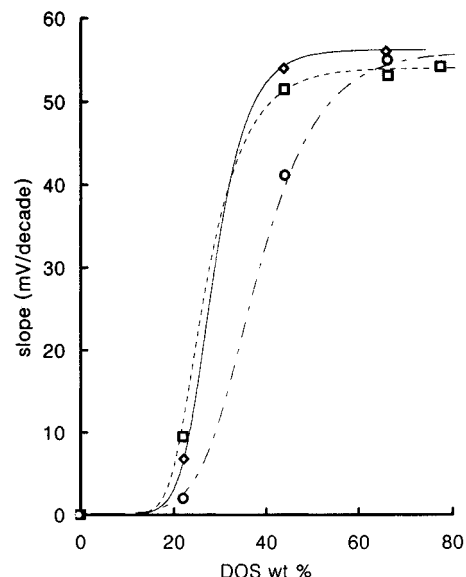


Figure 4. Variation of the response slopes of PU20 (○), PU40 (◇), and PU60 (□)-based electrodes with plasticizer contents.

the lack of inherent anionic sites in type 1 membranes would have limited the ion exchange kinetics at the membrane/water interface, resulting in null or poor potentiometric response.³⁷ These possibilities were examined with type 2 and type 3 membranes.

As illustrated in the inset of Figure 2, the glass transition temperatures (T_g) of PU membranes are proportionally lowered with increasing plasticizer contents. Single T_g values of plasticized PU membranes, which were determined from the inflection point of DSC thermograms, indicate that plasticizer molecules and the strands of soft segments form a homogeneous phase.⁶ Plasticizer added to PU matrices also altered their apparent mechanical properties: PU20 and PU40 became flexible but were still opaque; PU60 became similar to highly plasticized PVC; and PU80 became flaccid.

Figure 4 demonstrates the effect of increasing plasticizer contents on the potentiometric responses of type 2 membranes; plots of their response slopes vs DOA contents were well depicted with sigmoidal functions. This type of sigmoidal curve has been observed by Oesch and Simon from the plots of response slopes vs ionophore concentrations with PVC-based membranes.⁸ The potentiometric responses of PVC-based membranes, however, are much less dependent on the plasticizer contents.⁸ On the contrary, the potentiometric performance of PU-based membranes improved marginally with increasing valinomycin concentration (type 1 membranes) but drastically with increasing plasticizer contents (type 2 membranes). Apparently, the plasticizer added to PU increases the free carrier concentration in the membrane by dissolving carrier molecules dispersed about the partially structured soft segments or semicrystalline hard segments into the uniform rubbery phase. As expected, PU matrices with higher soft segment contents exhibited near-Nernstian response (e.g., slope > 50 mV/decade) with smaller amounts of plasticizer: 66 wt % for PU20, 44 wt % for PU40 and PU60, and 22 wt % for PU80. Plasticizer added to type 2 membranes also improved their potassium selectivity over sodium (see Table 1). However, no specific correlation between the response times of type 2 membranes (7.0 ± 1.5 s) and their DOA contents was observed.^{39–41} If the formation of electrode potential is bound to the surface of the electrode,³⁸ and the thickness of double layer formed at the water/

- (34) Brunette, C. M.; Hsu, S. L.; MacKnight, W. J. *Macromolecules* **1982**, *15*, 71–77.
- (35) Coleman, M. M.; Skrovanek, D. J.; Hu, J.; Painter, P. C. *Macromolecules* **1988**, *21*, 59–65.
- (36) Lee, H. S.; Wang, Y. K.; MacKnight, W. J.; Hsu, S. L. *Macromolecules* **1988**, *21*, 270–273.
- (37) Buck, R. P.; Nahir, T. M.; Cosofret, V. V.; Lindner, E.; Erdösy, M. *Anal. Proc. Anal. Commun.* **1994**, *31*, 301–312.
- (38) Pungor, E. *Electroanalysis* **1996**, *8*, 348–352.
- (39) Spichiger, U. E.; Citterio, D.; Bott, M. *Proc. SPIE-Int. Soc. Opt. Eng.* **1995**, *2508*, 179–189.

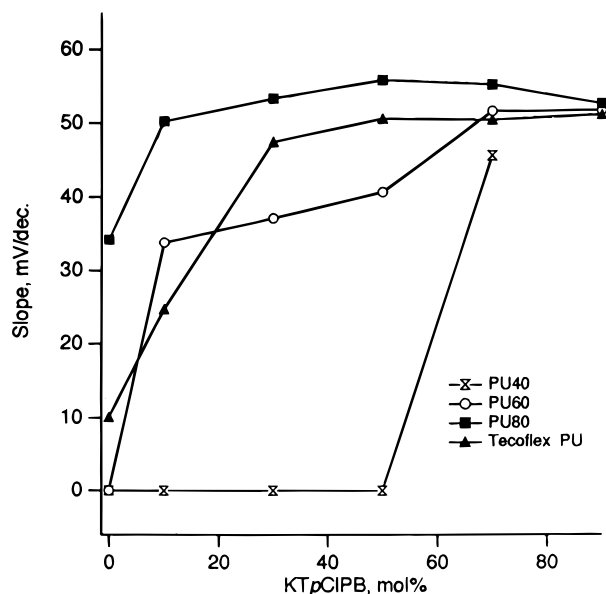


Figure 5. Variation of the response slopes of type 3 membrane-based electrodes with KTpCIPB concentrations.

membrane surface is uniform under our experimental condition,^{40,41} the response times of PU-based membranes may not depend on the fluidity of the bulk membrane [cf. $t(\Delta E/\Delta t)$ of PVC-based membrane ≈ 6.5 s].³⁹

It is also plausible that the increased potentiometric response of type 2 membranes may have resulted from some anionic impurities contained in DOA plasticizer (purity specification > 99%). For example, Bühlmann et al. recently reported that anionic impurities contained in some commercial plasticizers (DOS and *o*-NPOE) cause significant potentiometric responses.⁴² A recent report of nascent protonated anionic sites in Tecoflex PU-based pH membrane may also have been the result of *o*-NPOE plasticizer.²⁶ In this study, however, no special efforts have been made to identify the presence or the role of such anionic impurities in plasticized PU membranes. Instead, we investigated the effect of deliberately added mobile anionic sites, T_pCIPB⁻, on the potentiometric properties of PU-based membranes (type 3 membranes).

Figure 5 shows the influence of varying KTpCIPB concentrations on the responses of type 3 membrane-based electrodes; the response slopes of the electrodes gradually improved with increasing KTpCIPB concentration. However, the effect was apparent only for the matrices that contain high levels of soft segments ($w_{\text{soft}} \geq 60$ wt %). As was observed with type 1 membranes, the response behavior of the Tecoflex PU-based type 3 membrane was similar to that of an aromatic PU membrane containing about 60–80 wt % soft segments. Apparently, appropriate amounts of lipophilic salt added to PU membranes facilitate the ion exchange process at the membrane/water interface, resulting in enhanced potentiometric performance.³⁷ It is also possible that lipophilic additive helped the dissolution of neutral carriers in the membrane. Considering that additional incorporation of mobile anionic sites into the membranes with fixed anionic

sites (e.g., plasticized PVC or silicone rubber) results in marginal improvements in their potentiometric performance, the large increase in potentiometric responses observed with type 3 membranes may suggest the presence of a negligible level of anionic sites in PU matrices.^{6,19,37,44}

Small amounts of KTpCIPB (10 and 80 mol %, respectively, with respect to the ionophore) added to PU20 and PU40 matrices yielded waxy membranes. It seems that KTpCIPB promotes phase separation by disrupting the hydrogen-bonded cross-links in PU matrices.^{34–36} As the contents of hard segments increase, fractions of KTpCIPB participating in such an interaction in the vicinity of urethane groups would also increase.⁴³ Owing to this type of chemical interaction between mobile anionic sites and urethane chains, plasticizer-free PU membranes could be prepared only with the matrices with high soft segment contents ($w_{\text{soft}} \geq 60$ wt %). We investigated the potentiometric performance of other ion-selective membranes based on PU60 and Tecoflex PU incorporating ETH 1001 (Ca²⁺-selective neutral carrier), ETH 2120 (Na⁺-selective), or (trifluoroacetyl)-*p*-butylbenzene (CO₃²⁻-selective) with and without lipophilic salt (KTpCIPB or TDMACI); these membranes also exhibited near-Nernstian response only in the presence of an appropriate amount of lipophilic salt.

To optimize the performance of PU-based membranes, varying amounts of DOA plasticizer were added to the PU membranes containing 50–70 mol % KTpCIPB (type 4 membranes). As can be seen from Table 1, PU-based ISE membranes with reduced plasticizer contents (<66 wt %) may be prepared with the matrix that contain at least 60 wt % soft segments. If we aim to develop PU-based ISE membranes for clinical use, the level of plasticizer could be further optimized to increase their biocompatibility. For instance, Espadas-Torre and Meyerhoff reported that valinomycin-based Tecoflex PU membranes with 8 wt % DOS and 60 mol % KTpCIPB exhibit adequate sensitivity and selectivity for use in blood potassium determinations.²⁴ PU membranes containing more than 80 wt % soft segments were too flaccid to use for practical purposes.

CONCLUSION

To investigate the effect of matrix structure on the potentiometric properties of PU-based membranes, emf responses of PU-based membranes were examined as a function of soft segment contents in aromatic PU matrices. PUs with $w_{\text{soft}} > 60$ wt % exhibited appreciable potentiometric responses (slope < 35 mV/decade) in the absence of plasticizer and/or lipophilic additive. The apparent effect of adding plasticizer to PU-based membranes was comparable to that resulting from an increase of free carrier concentration in normal PVC-based membranes. The response times of PU-based membranes ($t(\Delta E/\Delta t) = 7.0 \pm 1.5$ s) were not dependent on the plasticizer contents. The large increase in potentiometric responses upon adding lipophilic additive may indicate the lack of inherent anionic sites in PU-based membranes. Owing to the chemical interaction between the lipophilic additive and PU matrix, plasticizer-free ISE membranes could be formulated with the PU matrix containing $w_{\text{soft}} > 60$ wt %. PUs composed of $60 \leq w_{\text{soft}} < 80$ wt % are recommended as the matrix

(40) Lindner, E.; Tóth, K.; Pungor, E.; Morf, W. E.; Simon, W. *Anal. Chem.* **1978**, *50*, 1627–1631.

(41) Huser, M.; Gehrig, P. M.; Morf, W. E.; Simon, W.; Lindner, E.; Jeney, J.; Tóth, K.; Pungor, E. *Anal. Chem.* **1991**, *63*, 1380–1386.

(42) Bühlmann, P.; Yajima, S.; Tohda, K.; Umezawa, Y. *Electrochim. Acta* **1995**, *40*, 3021–3027.

(43) IR spectra of thin PU60 films cast with and without KTpCIPB showed that the intensity of free C=O stretching band at 1728 cm⁻¹ significantly decreases with increasing KTpCIPB concentrations.

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

for fabricating ISE membranes with no or low plasticizer content. Such membranes also have appropriate mechanical properties.

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