Physical and Potentiometric Properties of Polyurethane-Based Cation-Selective Membranes

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ABSTRACT: Lipophilic salts based on tetraphenylborate derivatives [e.g., potassium tetrakis(p-chlorophenyl)borate (KTpClPB), sodium tetraphenylborate (NaTPB), and cesium tetrakis(3-methylphenyl)borate are essential ingredients used in the preparation of solvent polymeric cation-selective membranes. The effects of such lipophilic salts on the physical properties of a polyurethane (PU) matrix comprising 4,4′-diphenyl-methane diisocyanate, 1,4-butanediol, and poly(tetramethylene ether glycol) were examined. Differential scanning calorimetry measurements revealed that the sodium and potassium salts doped in PU increased the glass-transition temperatures (T_g) of the matrix, while the film containing cesium salt exhibited slightly decreased T_g. The temperature dependence of the ionic conductivity for PU60 films doped with KTpClPB is well described by the Arrhenius-type equation, and that doped with NaTPB is described by the Vogel–Tammann–Fulcher (VTF)-type equation. The temperature dependence of the ionic conductivity on the VTF-type equation suggests that the transport of sodium ions in the PU60 matrix is more strongly coupled to the soft segmental motion, and potassium ions are decoupled from the polymer host and transported by activated hopping. The effect of added salt on the internal structure of PU membranes was investigated by measuring the ratio between the free and hydrogen-bonded C=O bands at 1703 and 1730 cm^{-1}, respectively. The results showed that the ether oxygens in the soft segment chains are strongly coupled to the potassium or sodium, but much less to cesium. The potentiometric properties of these lipophilic additive doped PU membranes were characterized by incorporating valinomycin and 4-*tert*-butylcalix[4]arene-tetraacetic acid tetraethylester as potassium- and sodium-selective ionophores, respectively. Their response behavior could be explained by the observed physical characteristics. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 618–625, 2001

Key words: physical and potentiometric properties; polyurethane; cation-selective membranes; lipophilic salts

INTRODUCTION

Various types of synthetic polymers are widely used to immobilize or entrap natural and artificial receptors and to impart molecular recognition capability to a sensitive transducer of chemical sensors.[1,2] A poly(vinyl chloride) (PVC)-based ion-selective membrane is a typical example: it is readily prepared by incorporating small amounts of electroactive compounds (1–2 wt % of ionophore and lipophilic salts) into the solvent polymeric matrix comprising one part high molecular weight PVC and two parts plasticizer.[3] In the last three decades, numerous articles contributed to establishing the realm of ISE-based analysis, providing operational theories, newly developed ionophores, and various types of modified membranes for challenging applications.[4–6]

While the functional aspect of ISE was the main research interest in the study of ion-selective membranes, the fundamental physicochemical properties of solvent polymeric matrices also attracted some attention.[7–19] For example, a number of research groups extensively measured the mechanical, thermal, and electrical properties of various kinds of overplasticized PVC films and the behavior of ionic species (e.g., dissociated lipophilic salts and ion-ionophore complexes) incorporated in them and attempted to use the observed results to find improved membrane systems for ISEs and biosensors.[7–20]

Polyurethane (PU) is another polymer matrix popularly used for formulating chemical sensor membranes for biomedical applications. Nam and Cha noted that PVC-based membranes suffer from protein and platelet adsorption and become inoperative in a short time.[21] Several research groups reported that the ISE membranes based on medical-grade PUs exhibit significantly reduced blood clotting, platelet adhesion, and host inflammatory response in the *in vivo* application, provided that their compositions are properly optimized.[22–29] Hydrophilic PUs are also frequently used with PU-based membranes or other solid-state electrodes to improve their biocompatibility and immobilization of bioactive reagents.[30,31] Furthermore, PU-based membranes are, in general, better suited for fabricating miniaturized all solid-state ISEs because of their stronger adhesion to solid substrates than that of PVC-based membranes.[21,23,28] We also recently showed that some aromatic PU membranes doped with an equimolar amount of cationic and anionic lipophilic additives can be used for fabricating liquid junction-free reference electrode. These advantages steadily increase the use of PU membrane-based chemical sensors in the field of biomedical applications.

Unlike the plasticized PVC membranes, little is known about the physical and chemical nature of PU-based membranes.[21] Consequently, systematic electrochemical research on the ion-selective membranes was conducted by fabricating them with a series of 4,4′-diphenylmethane diisocyanate (MDI)-based aromatic PUs having different soft/hard-segment ratios ($w_{soft}/w_{hard} = 0.8–0.2$).[29] The study showed that plasticizer-free PU-based ISE membranes exhibit near-Nernstian response only in the presence of an appropriate lipophilic additive, which is concomitant with the phase boundary potential theory.[4] Unfortunately, the physical strengths of PU-based membranes containing a lipophilic additive such as potassium tetrakis-(p-chlorophenyl)borate (KTpClPB) become waxy and very weak beyond a certain level. The observed phenomenon was more pronounced in the hard segment rich PUs (e.g., $w_{hard} \geq 60\%$), indicating that the lipophilic additive incorporated in the membrane significantly disrupted the internal structures of the PU matrix. While the use of a lipophilic salt in the formulation of a PU-based ISE membrane can be essential,[29,32] the effect of added lipophilic salt on the internal structure of the PU matrix is not clearly understood. Specifically, no data were provided if the varying physical properties of the lipophilic salt-doped PU membranes had any relations with their resulting potentiometric characteristics.

This study investigates the relationship between the physical and potentiometric properties of the PU-based membranes. A series of experiments are conducted to learn the effect of lipophilic salts (i.e., sodium, potassium, and cesium tetrakisphenyl borate derivatives) on the T_g, conductivity, and hydrogen bonding of an MDI-based PU using differential scanning calorimetry (DSC), an impedance analyzer, and FTIR. The observed physical properties of the lipophilic salt-doped PU-based membranes are discussed in relation to their chemical sensor applications.

EXPERIMENTAL

Reagents

The reagent sources were as follows: poly(tetramethylene ether glycol) (PTMEG) with 2000 mo-

(A) MDI-based polyurethane (PU60)

(B) lipophilic additives
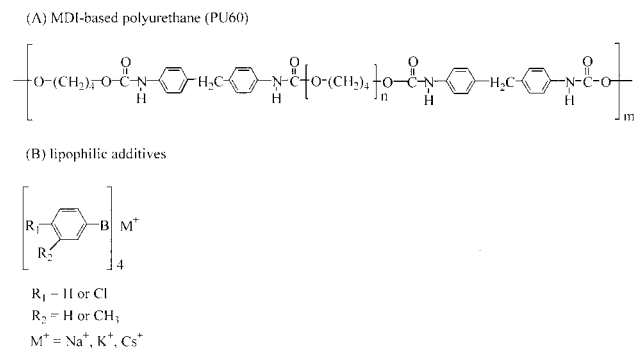
R₁ = H or Cl
R₂ = H or CH₃
M⁺ = Na⁺, K⁺, Cs⁺

Figure 1 The structures of (A) polyurethane and (B) lipophilic additives examined in this work.

lecular weight was from Aldrich (Milwaukee, WI); MDI was from Kanto Chemical Co. (Tokyo); 1,4-butanediol (BD), KTpClPB, sodium tetraphenylborate (NaTPB), cesium tetrakis(3-methylphenyl)borate (CsTMPB), valinomycin, and 4-*tert*-butylcalix[4]arene-tetraacetic acid tetraethylester (sodium ionophore X) were from Fluka (Büch, Switzerland). All other solvents and chemicals were analytical reagent grade.

Preparation of Polymer

The aromatic PUs shown in Figure 1 were synthesized as previously reported.[28] This required three steps: 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 capping of unreacted isocyanates with absolute methanol. The reaction was carried out under a dry nitrogen atmosphere at 60°C for 5 h, except when BD was added to the prepolymer in an ice bath. In estimating the relative compositions of MDI, BD, and PTMEG, a given weight percentage of PTMEG in those three components was approximated as the contents of soft segments in the synthesized PU, and the molar ratio between MDI and total diols was adjusted to 1 : 1. These PUs are denoted as PUnn (e.g., PU20, PU40, PU60, and PU80), where nn indicates the weight percentage of soft segment contents (w_{soft}) in the synthesized PU. For this experiment, we used PU60 as our model matrix.

FTIR Measurements

The FTIR measurements were made on the films produced by casting a THF solution containing 10 mg PU and proper amounts of lipophilic additives in a glass ring (22-mm i.d.) on a glass plate. The solvent was slowly evaporated in a vacuum dessicator for 24 h at 25°C. IR spectra were recorded at ambient temperature using a Nicolet Magna 550 FTIR spectrophotometer with a wave number resolution of 4 cm⁻¹.

DSC Measurements

Samples for DSC were prepared by dissolving PU60 and lipophilic salts (10-mg total weight) in THF and casting the solution in a glass ring (11-mm i.d.) placed on a slide glass. Thermograms for PU60 films were obtained using a Shimadzu TA-50 WSI DSC. The sample chamber was purged with dried helium during the measurement. Each hermetically sealed sample was first cooled from room temperature to −130°C, and then DSC measurements were made over the temperature range of −110 to 250°C at a heating rate of 10°C/min.

Conductivity Measurements

The ion conductivity measurements were made using an Hewlett Packard 4192A LF impedence analyzer over the temperature range of 20–110°C. Sample films cast in the 22-mm i.d. glass ring were prepared by evaporating the THF solvent from the solution containing 50 mg of PU60 and varying amounts of lipophilic additives (1.5, 2.0, and 2.5 wt % KTpClPB and 2.5 wt % NaTPB and CsTMPB). The ionic conductivities of the PU60 films, which were sandwiched between two stainless steel electrodes with 20 N/cm² of applied pressure, were measured while increasing the temperature at a rate of 1°C/min.

Potentiometric Evaluation of PU-Based Membranes

Ion-selective membranes were prepared by incorporating 1 wt % of valinomycin or sodium ionophore X as an ionophore and 0, 30, 70, 100, and 200 mol % of KTpClPB, NaTPB, or CsTMPB with respect to the content of ionophore as a lipophilic additive into the PU60 matrix. The membrane cocktails were prepared by dissolving all components in 5 mL of THF. These cocktail solutions were then poured into a glass ring (22-mm i.d.) placed on a slide glass or Teflon plate and dried for 1 day at room temperature. Small disks were punched from the cast films and mounted in Philips electrode bodies (IS-561, Glasblaserei Möller, Zürich) containing 0.1M KCl as an internal filling solution. All electrodes were presoaked in deionized water over 24 h before the electromotive force
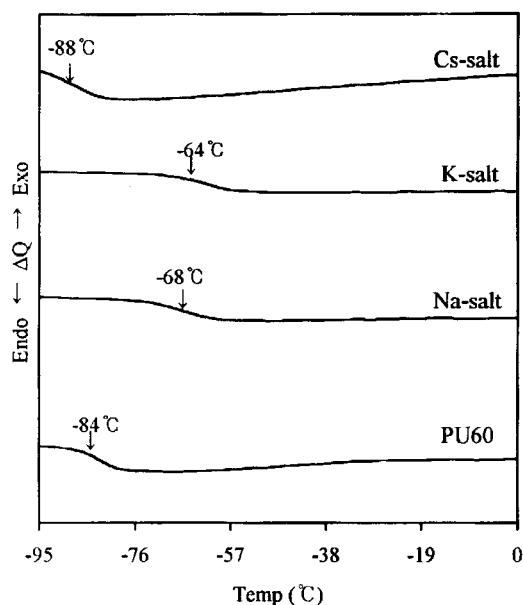
Figure 2 DSC thermograms showing the effect of added lipophilic additives on the glass-transition temperatures of PU60 films. Each film sample contains 10 wt % (or 1.0 mg) of sodium tetraphenylborate (NaTPB), potassium tetrakis(p-chlorophenyl borate) (KTpClPB), and cesium tetrakis(3-methylphenyl borate) (Cs-TMPB).

measurements. Potentiometric evaluation of the electrodes was performed in a 0.05M Tris-HCl buffer solution (pH 7.2) as described previously using a static arrangement.[29]

RESULTS AND DISCUSSION

DSC Analysis

Figure 2 shows the effect of added lipophilic additives on the glass-transition temperatures of PU60 films. Each film contained 10 wt % (or 1.0 mg) of NaTPB, KTpClPB, or CsTMPB (cf. Fig. 1). These compounds are the most frequently used lipophilic additives for formulating solvent polymeric ion-selective membranes.[33] While the films containing sodium and potassium salts exhibited substantially increased T_g values from −84 to −68 and −64°C, respectively, the T_g with cesium salt decreased slightly to −88°C.

Previous studies on the thermal behavior of PU doped with lithium salts (e.g., $LiClO_4$ and $LiCF_3SO_3$) showed that the glass-transition temperature of PU increases with increasing salt concentrations.[34–37] This increase occurs because al-

kali metal salts in the soft segments of PU behave like those doped in polyether-type polymers [e.g., poly(ethylene oxide), poly(propylene oxide), and poly(ethylene glycol)], forming solid polymer electrolytes (SPEs).[38–42] The dissociated alkali metal ions in the soft-segment domains are coordinated to the ether oxygens and partially lock the local motion of the polymer segments.[38–41] resulting in increased T_g values.[34,35] Thus, the increase in the T_g values of the NaTPB- and KTpClPB-doped PU60 films indicated that these lipophilic salts undergo an appreciable degree of dissociation in the PTMEG soft-segment domain, constituting a good SPE system. On the other hand, the slight decrease in the T_g of the CsTMPB-doped PU60 film suggests that the salt caused a plasticizing effect. This decrease may be explained if we assume the neutral contact ion pair is the dominant form of cesium salt in the PTMEG domains.[35]

Conductivity Measurements

Alkali metal salts added to PU to make SPEs are usually about 0.1–2.0 mmol/g of PU. However, because the amount of lipophilic additives used for formulating polymeric ion-selective membranes is in general less than 2 wt % (0.04 mmol/g of PU60 for KTpClPB), we examined the conductivity behavior of PU60 films containing 1.5–2.5 wt % lipophilic salts in this experimental work. Figure 3(A) illustrates the conductivity behavior as a function of the reciprocal temperature for the PU60 films having three different concentrations of KTpClPB (1.5, 2.0, and 2.5 wt %). As the concentration of this dopant increased from 1.5 to 2.5 wt %, the bulk conductivity increased by 10–50 times within the temperature range of 25–110°C.

Figure 3(B) shows that the conductivities of PU films doped with 2.5 wt % NaTPB and KTpClPB ($\sigma \sim 2 \times 10^{-7}$ to 6×10^{-6} S cm^{-1}) are about 25–120 times greater than that of the CsTMPB-doped film ($\sigma \sim 8 \times 10^{-9}$ to 5×10^{-8} S cm^{-1}) in the given temperature range. This result is consistent with the thermal behavior discussed earlier; cesium salt is less dissociated and has lower mobility in the PU60 matrix. The temperature dependence of the ionic conductivity for PU60 films doped with KTpClPB is well described by the Arrhenius-type equation, and that with NaTPB is described by the Vogel–Tammann–Fulcher (VTF)-type equation.[38,39] Thus, the transport of sodium ions in the PU60 matrix is more strongly coupled to the soft-segmental motion whereas potassium ions are decoupled from the
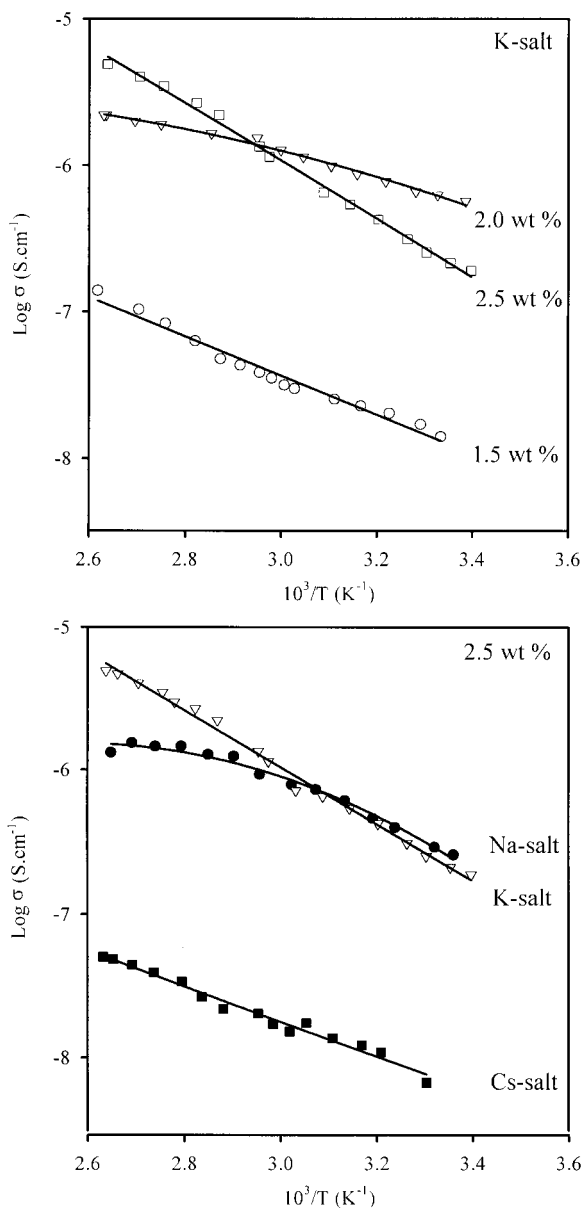
Figure 3 The conductivity behavior of PU60 films containing three different concentrations of KTpClPB (1.5, 2.0, and 2.5 wt %) and 2.5 wt % of three different salts (NaTPB, KTpClPB, and CsTMPB).

FTIR Measurements

The effects of added lipophilic salts on the internal structure of the PU60 film were investigated by analyzing the spectral changes in the C=O and N—H stretching vibrational regions as a function of the salt concentration and tempera-

ture. The C=O and N—H stretching vibrations of PU sensitively indicate the localized hydrogen-bonding environment, resulting in well-resolved free and hydrogen-bonded peaks for each vibrational mode. For PU60 the C=O stretching vibration is split into two peaks at 1703 and 1730 cm^{-1} and the C—H vibration is split at 3340 and 3410 cm^{-1}; the low and high wave number peaks in each band correspond to the hydrogen-bonded and free stretching mode, respectively.

To examine the effect of added lipophilic salts on the internal hydrogen bonding, the fraction of the free C=O peak area ($X_{\text{free}}^{\text{C=O}}$) was measured using the equation,

$$X_{\text{free}}^{\text{C=O}} = \frac{A_{\text{free}}}{1 + rA_{\text{H bond}}} \quad (1)$$

where A_{free} and $A_{\text{H bond}}$ are the integrated intensity of the free and hydrogen-bonded C=O peak, respectively, and r is the ratio of the corresponding absorption coefficients (i.e., $r = \varepsilon_{\text{free}}/\varepsilon_{\text{H bond}}$). The experimentally determined ratio for similar PU films is close to 1.0.[43] Figure 4 shows a plot of the $X_{\text{free}}^{\text{C=O}}$ versus the weight percentage of salt incorporated: while the fractions of the free C=O for NaTPB- and KTpClPB-doped PU60 films decreased significantly with increasing salt concen-
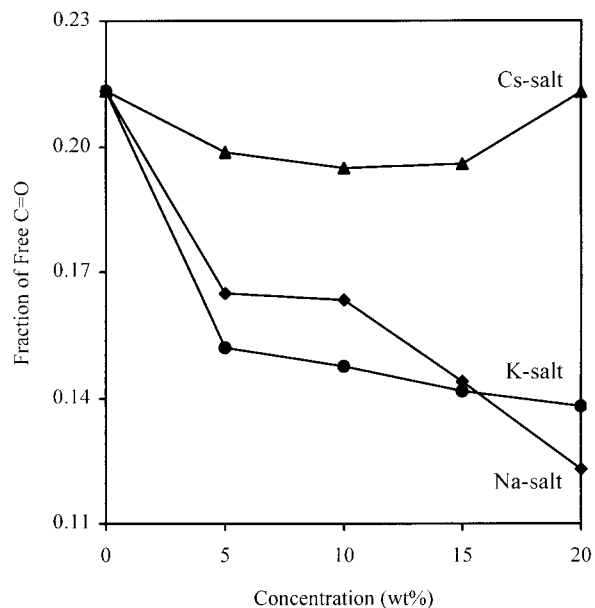
polymer host and transported by activated hopping.[35]

Figure 4 The fractions of the peak area of the free C=O stretching vibration at 1730 cm^{-1} as a function of salt concentration in PU60 films containing NaTPB, KTpClPB, and CsTMPB.

tration, those for the CsTMPB-doped varied little. Ferry et al. reported that lithium perchlorate doped in PU causes $X_{\text{free}}^{C=O}$ to decrease.[34] They thought that the rearranged hydrogen bonding between N—H and C=O groups reduces the $X_{\text{free}}^{C=O}$ values as the ether oxygens in the soft-segment chains are coordinated to the dissociated alkali metal cations. On the other hand, the relatively constant $X_{\text{free}}^{C=O}$ values in the CsTMPB-doped PU60 film may support the conclusions derived from the DSC and conductivity measurements: the dissociation of cesium salt in PU60 matrix is much smaller than those of the sodium and potassium salts.

Potentiometric Evaluation of PU60-Based Potassium- and Sodium-Selective Membranes

Potassium- and sodium-selective membranes were fabricated by incorporating suitable ionophores (i.e., 1 wt % of valinomycin and sodium ionophore X, respectively) and varying concentrations of lipophilic salts (0, 30, 70, 100, and 200 mol % of NaTPB, KTpClPB, or CsTMPB with respect to the ionophore) into the PU60 matrix. The potentiometric responses of these membranes to potassium and sodium are shown in Figures 5 and 6 and summarized in Tables I and II.

The PU60-based potassium-selective membranes exhibited negligible response slopes (21–24 mV/decade) in the absence of lipophilic salts, indicating that the PU matrix used in this study contained little anionic impurities. The addition of 30–70 mol % of lipophilic salts resulted in Nernstian responses in the 10^{-4}–$10^{-1}M$ range. However, the response slopes of valinomycin-doped PU60 membranes decreased drastically when 100–200 mol % of KTpClPB was incorporated but decreased to a lesser degree with the same concentrations of NaTPB and CsTMPB.

The neutral carrier valinomycin (val) doped in the membrane would bind the dissociated alkali metal cations (M$^+$) from the lipophilic salts, forming M–val$^+$ complexes. Buck et al. found that the concentration of cation–ionophore complexes should be less than that of the total anionic sites for the membranes to exhibit an appreciable potentiometric response.[20] They also observed that the excess lipophilic additive incorporated is spontaneously lost from the membrane until the unity neutral carrier/anionic site ratio is achieved. Such an effect is more pronounced with NaTPB than KTpClPB because the K–val$^+$TpClPB$^-$ ion pair has higher lipophilicity.
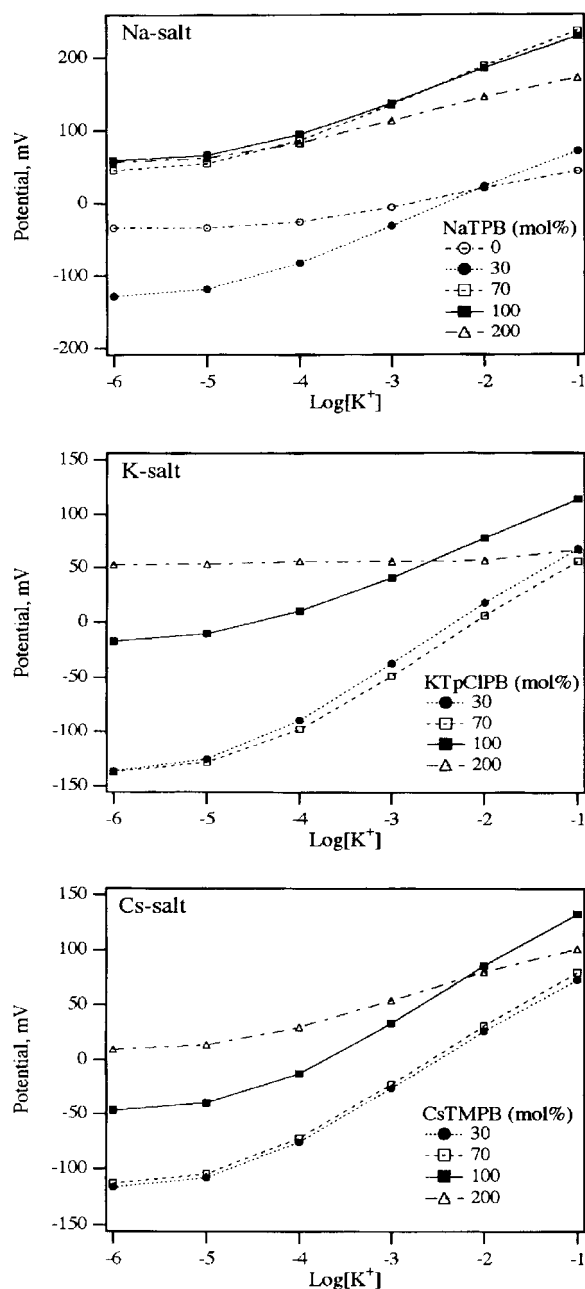

Figure 5 Calibration plots of varying the concentration of potassium for the PU60-based membranes doped with 1 wt % valinomycin as an ionophore and 0, 30, 70, 100, and 200 mol % of lipophilic additive with respect to the ionophore for NaTPB, KTpClPB, and CsTMPB.

Bearing these results in mind, we may interpret the observed potentiometric behavior of PU60-based membranes.

As the DSC, conductivity, and FTIR measurements indicated, potassium and sodium containing lipophilic salts have a higher degree of dissociation
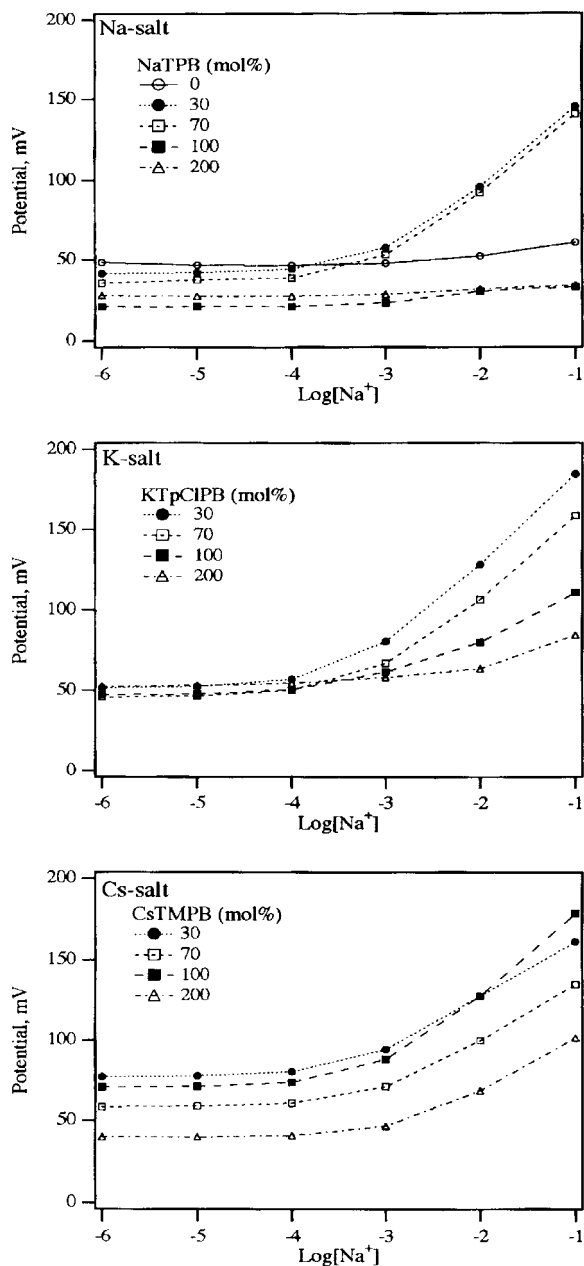
Figure 6 Calibration plots of varying the concentration of sodium for the PU60-based membranes doped with 1 wt % 4-*tert*-butylcalix[4]arene-tetraacetic acid tetraethylester as an ionophore and 0, 30, 70, 100, and 200 mol % of lipophilic additive with respect to the ionophore for NaTPB, KTpClPB, and CsTMPB.

in the PU60 matrix than cesium salt. Thus, the potassium ion solubilized in the soft-segment domain of PU60 would be stabilized by forming K–val$^+$ complexes, decreasing the effective concentration of free ionophore below the limiting level when 100 mol % of KTpClPB is added to the mem-

Table I   Potentiometric Properties of PU60 Membranes Doped with 1 wt % Valinomycin

Lipophilic Additive	Composition[a] (mol %)	Slope[b] (mV/decade)	Detection Limit ($-\log[K^+]$)
NaTPB	0	21.7	4.4
	30	51.4	4.9
	70	50.3	4.8
	100	44.9	4.8
	200	29.7	4.9
KTpClPB	30	52.4	4.9
	70	51.5	4.8
	100	34.9	4.7
	200	—	—
CsTMPB	30	50.2	4.8
	70	51.0	4.8
	100	48.9	4.7
	200	23.8	4.9

[a] The concentration is with respect to the content of valinomycin.
[b] Range = 10^{-4}–10^{-1} M.

brane.[44] On the other hand, the loss of response slopes with the NaTPB-doped membrane was less severe than that with the potassium salt doped membrane, probably because of the spontaneous loss of the sodium salt from the membrane. Buck et al. suggested that the slow decrease in sensitivity is the main advantage of using NaTPB for the ion-

Table II   Potentiometric Properties of PU60 Membranes Doped with 1 wt % Calix-4-Arene

Lipophilic Additive	Composition[a] (mol %)	Slope[b] (mV/decade)	Detection Limit ($-\log[Na^+]$)
NaTPB	0	—	—
	30	34.0	3.8
	70	34.5	3.8
	100	—	—
	200	—	—
KTpClPB	30	43.1	3.9
	70	36.4	3.9
	100	19.7	3.9
	200	—	—
CsTMPB	30	27.6	3.9
	70	25.0	3.8
	100	35.6	3.8
	200	20.4	3.7

[a] The concentration is with respect to the content of calix-4-arene.
[b] Range = 10^{-4}–10^{-1} M.

selective membrane.[20] However, the effect of cesium salt on the response slope may be related to its low dissociation in the PU membrane. Hence, the use of CsTMPB for PU-based membranes may be advantageous if the longevity and stability of the sensor are the main concerns, because the cesium salt is chemically more stable than NaTPB while providing Nernstian responses.

As shown in Figure 6 and Table II, the potentiometric performance of PU-based sodium-selective membranes is generally poor, providing a non-Nernstian response with high detection limits. The conductivity measurements suggest that the transport of sodium in the PU matrix is coupled to its soft-segmental motion. Hence, we may expect that the sodium-selective neutral carrier doped in PU-based membranes would exhibit limited ion-carrying ability, competing against the nonspecific sodium binding polyether chains. This is the main disadvantage of PU-based membranes with no or reduced plasticizer: their cation selectivities over sodium, when it is an interfering ion, are generally much poorer than those of the corresponding PVC-based membranes.

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