Noncyclic Polyethers containing Sulphur Atoms: a Novel Type of Neutral Carrier for Ion-selective PVC Membrane Electrodes

Hideki Sugihara,* Tatsuhiro Okada, and Kazuhisa Hiratani

Industrial Products Research Institute, Higashi 1-chome, Yatabe-machi, Tsukuba-gun, Ibaraki 305, Japan

PVC membrane electrodes based on noncyclic polyethers containing sulphinyl groups exhibit appreciable selectivity for Ca^{2+} relative to Mg^{2+}, alkali metal ions, and H^+.

A number of neutral carriers for ion-selective electrodes have been reported so far, such as noncyclic polyether–diamides,[1] cyclic polyether–diamides,[2,3] crown ethers,[4] and bis(crown ethers).[5] However, little attention has been paid to noncyclic polyethers containing sulphur atoms as neutral carriers for ion-selective electrodes.[6] In this paper we report the potentiometric ion-selectivity of polymeric membrane electrodes based on newly synthesized polyethers containing sulphur atoms.

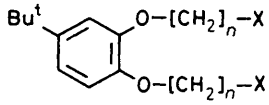
1,2-Bis(3-phenylsulphinylpropoxy)-4-t-butylbenzene (**1**) was obtained from the reaction of 1,2-bis(3-chloropropoxy)-4-t-butylbenzene with sodium benzenethioxide followed by sodium bromite oxidation, and purified by silica gel column chromatography.† Other polyether–disulphinyl compounds (**2**)—(**5**) were prepared and purified in a similar manner.

The polymeric membranes for the ion-selective electrodes were cast from tetrahydrofuran solutions of 3% (w/w) polyether, 69% 2-nitro-l-octyloxybenzene, 27% poly(vinyl chloride) (PVC), and 1% potassium tetrakis(4-chlorophenyl)-borate. The e.m.f. measurements were carried out at 25 °C; the composition of the electrochemical cell being Ag/AgCl/

† (**1**): Colourless oil; $\nu_{max.}$ (neat) 1040 cm^{-1} (S=O); δ_H (60 MHz, $CDCl_3$) 1.30 (9H, s, $C[CH_3]_3$), 1.90—2.40 (2H, m, $CH_2CH_2CH_2$), 2.90—3.20 (2H, m, $CH_2CH_2S[O]$), 4.13 (2H, t, OCH_2CH_2), 6.87—7.98 (13H, m, aromatic).

Table 1. Selectivity coefficients for PVC membrane ion-selective electrodes based on (**1**)—(**6**).

	k^{Pot}(Ca/M)				
Compound	Mg^{2+}	Li^+	Na^+	K^+	H^+
(**1**)	8.5×10^{-3}	9.3×10^{-3}	1.0×10^{-3}	3.0×10^{-3}	5.4×10^{-2}
(**2**)	3.3×10^{-2}	4.7×10^{-2}	2.0×10^{-2}	3.3×10^{-1}	3.4×10^{3}
(**3**)	1.5×10^{-2}	4.9×10^{-2}	3.6×10^{-2}	4.3×10^{-2}	4.1×10^{-1}
(**4**)	6.8×10^{-3}	3.6×10^{-2}	7.4×10^{-3}	1.6×10^{-2}	2.6
(**5**)	6.8×10^{-2}	2.1×10^{-1}	2.7×10^{-2}	1.6×10^{-2}	1.9×10^{2}
(**6**)	1.5×10^{-1}	1.2	8.5×10^{1}	1.1×10^{5}	8.5×10^{2}



(**1**) n = 3, X = S(O)Ph
(**2**) n = 3, X = S(O)C_8H_{17}-n
(**3**) n = 2, X = S(O)Ph
(**4**) n = 2, X = S(O)CH_2Ph
(**5**) n = 2, X = S(O)C_8H_{17}-n
(**6**) n = 3, X = SPh

10^{-3} M $CaCl_2$/PVC membrane/sample solution/0.1 M NH_4NO_3/sat. KCl/AgCl/Ag. The potentiometric selectivity coefficients were determined using a separate solution method.

The selectivity coefficients for Ca^{2+} relative to the ion M [k^{Pot}(Ca/M)] in the PVC membrane electrodes based on (**1**)—(**6**) are listed in Table 1. The calibration plots for the electrode based on (**1**) showed a near-Nernstian response (slope 28 mV decade^{-1}) and good detection limits (less than 10^{-5} mol dm^{-3}) for Ca^{2+}. The electrodes based on sulphinyl compounds (**1**)—(**5**) exhibit appreciable selectivity for Ca^{2+} relative to other metal ions. The response time of the electrodes to change in Ca^{2+} concentration was less than 2 min, and the electrodes showed almost the same e.m.f. response after 1 week's exposure to 10^{-3} M $CaCl_2$ solution. On the other hand, the electrodes based on corresponding sulphenyl compounds in place of sulphinyl compounds do not exhibit any Ca^{2+} selectivity. From these results it is suggested that the oxygen atoms of sulphinyl groups play an important role in the ion-selectivity. It should be noted that the electrodes based on (**1**) and (**3**), which have phenylsulphinyl terminal groups, showed selectivity for Ca^{2+} over H^+.‡ Therefore Ca^{2+} selective electrodes based on (**1**) and (**3**) may be of great practical use in medical applications.[7] Thus, noncyclic polyethers containing sulphur atoms may be used as ion sensing agents.

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‡ The high variability of selectivity was observed only for H^+. The cause of this behaviour seems to be that the sensing site for H^+ is different from that for the other cations.