Potentiometric SCN$^-$ Selectivity of Polymer Membranes with Fixed Organotin Compounds

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(Received September 6, 2001; CL-010877)

Novel polymer liquid membrane electrodes, in which the organotin compounds were fixed, were obtained by the reaction of PVC (poly(vinyl chloride)) with di-*n*-butyltin halide hydrides (^{n}Bu$_2$SnYH, Y = F, Cl, I, OMe). The improved liquid membrane electrodes displayed good potential stability and non-Hofmeister selectivity patterns. Furthermore, the highest degree of selectivity for the SCN$^-$ ion was achieved.

Organotin compounds are known as neutral carriers of PVC (poly(vinyl chloride)) liquid membrane electrodes (ion selective electrodes), and they are widely used for the development of new potentiometric anion-selective electrodes[1–14] in view of their low cost and easy availability. A variety of organotin compounds such as organotin halides,[1–8] carboxylates,[9] phenolates,[10] and bi-nuclear or trinuclear organotin compounds[11–14] are exploited as neutral carriers of the liquid membrane electrodes. The advantage of the electrodes based on organotin compounds is to exhibit non-Hofmeister selectivity patterns.[15] Problems incurred in using most organotin compound as neutral carriers are potential lowering and potential instability due to effusion of the neutral carrier from a potentiometric liquid membrane. The fixation of organotin compounds in PVC membranes by utilization of the chemical reactivity of organotin compounds is expected to improve the potential properties of the electrodes based on organotin compounds. The ionically activated organotin hydrides[16] seem to be attractive candidates for the reaction of polar multiple bonds. Therefore, we focused on ionically activated organotin hydride reagents bearing an electron-withdrawing group Y (Y = F, Cl, I, OMe), namely, di-*n*-butyltin halide hydrides (^{n}Bu$_2$SnYH).[17] In this context, we herein report the fixation of organotin compounds in PVC membranes by the reaction of PVC with di-*n*-butyltin halide hydrides (^{n}Bu$_2$SnYH, Y = F, Cl, I, OMe) to develop novel liquid membrane electrodes.

The reaction of PVC with ^{n}Bu$_2$SnYH was confirmed by the IR spectroscopy. The Sn–H absorption at 1867 cm^{-1} (the Sn–H stretching frequency)[18] disappeared after 60 minutes in the IR spectra, when ^{n}Bu$_2$SnClH was added to PVC in the THF solution. On the contrary, no decrease of the Sn–H absorption at 1837 cm^{-1} was observed [19] even after 90 minutes in the case of ^{n}Bu$_2$SnH$_2$.[20]

The potentiometric liquid membranes were formed by a casting method after the addition of plasticizer to the THF solution of the modified PVC with the ^{n}Bu$_2$SnYH (Y = F, Cl, I, OMe). The potentiometric liquid membrane modified with ^{n}Bu$_2$SnYH was composed of ^{n}Bu$_2$SnYH (22.5 wt%) as a neutral carrier and PVC (25.8 wt%) and bis(1-butylpentyl) adipate (BBPA) (51.7 wt%) as the plasticizer. Measurements were performed on cells of the type

Ag · AgCl / 0.01 M NaCl // membrane // sample
solution / 0.1 M CH_3COOLi // 3.3 M KCl / Ag · AgCl

at 25 ± 0.1 °C using a pH/mV meter equipped with a double-junction-type Ag–AgCl reference electrode. All water solution were buffered with tris(hydroxymethyl)aminomethane and H_2SO_4 to pH 7.5. The electrode using the thus-obtained potentiometric liquid membrane began to respond in anionic fashion as the concentration of the Cl$^-$ ion increased.

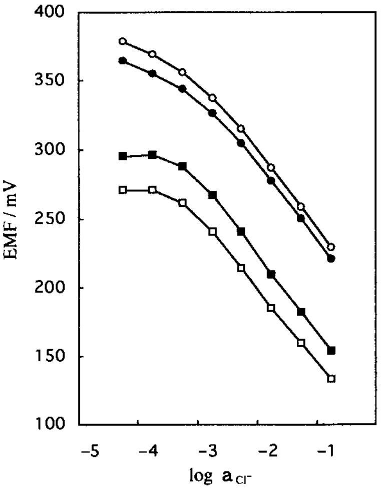

Figure 1. Effect of the conditioning times on calibration curves for modified electrode with Bu$_2$SnClH and the electrode based on Bu$_2$SnCl$_2$: (a); ● Bu$_2$SnClH (24 h), (b); ○ Bu$_2$SnClH (72 h), (c); ■ Bu$_2$SnCl$_2$ (24 h), (d); □ Bu$_2$SnCl$_2$ (72 h).

The modified electrode with ^{n}Bu$_2$SnClH displayed a good calibration curve for the Cl$^-$ ion over the activity range from $10^{-3.0}$ to $10^{-1.1}$ M (Figure 1 (a)). The slope was –56.9 mV/decade. This value was close to the theoretical Nernstian value (–59.2 mV/ decade).

No deterioration in the potential properties of this electrode was observed, even if the conditioning time was lengthened from 24 hours (Figure 1 (a)) to 72 hours (Figure 1 (b)). On the contrary, the electrode based on ^{n}Bu$_2$SnCl$_2$ showed potential lowering (Figure 1 (c) and (d)). ^{n}Bu$_2$SnCl$_2$ have no reacting ability for PVC. The potential lowering is likely to be caused by the effusion of ^{n}Bu$_2$SnCl$_2$ as a neutral carrier, because ^{n}Bu$_2$SnCl$_2$ is easily soluble in water. The electrodes using the modified PVC membranes by the reaction with other di-*n*-butyltin halide hydrides (^{n}Bu$_2$SnYH, Y = F, I, OMe) similarly displayed good calibration curves for the Cl$^-$ ion. The slope of the respective calibration curve was –59.9 (^{n}Bu$_2$SnFH), –64.4 (^{n}Bu$_2$SnIH), –52.1 (^{n}Bu$_2$Sn(OMe)H) mV/decade. All modified electrodes with ^{n}Bu$_2$SnYH showed response times of less than 5 min, although response times of up to 10 min were observed for the electrodes based on ^{n}Bu$_2$SnY$_2$ (Y = Cl, I, OMe).

Responses of the electrodes using modified PVC membrane by ^{n}Bu$_2$SnYH (Y = F, Cl, I, OMe) were measured for a

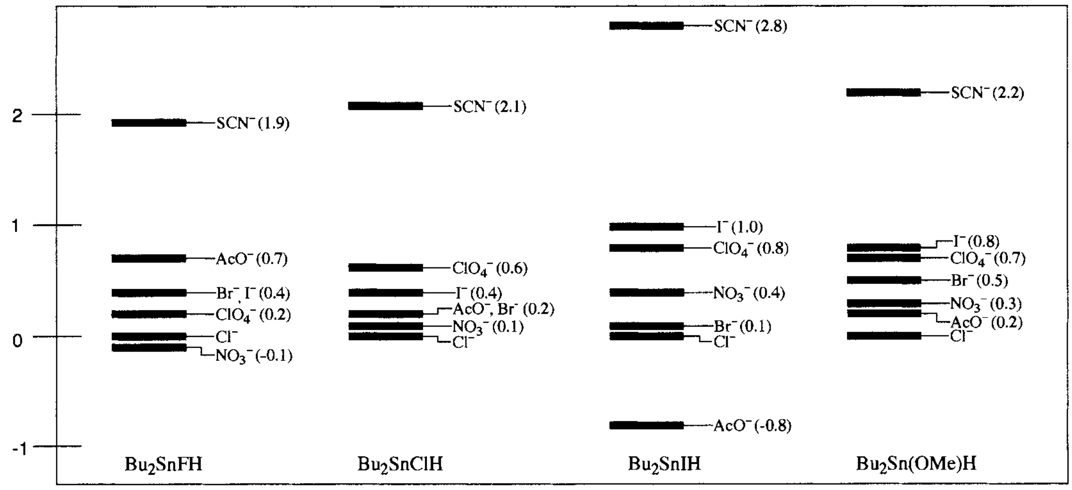

Figure 2. Selectivity coefficients of the modified electrodes with $^n\mathrm{Bu_2SnYH}$ (Y = F, Cl, I, OMe).

series of common monovalent anions X^-. The selectivity coefficients presented in Figure 2 were calculated from the E_{Cl^-} and E_{X^-} values in $10^{-1.0}$ M activity concentration. Selectivity coefficients for the Cl^- ion with respect to an interfering X^- ion ($\log k^{\mathrm{Pot}}_{\mathrm{Cl,X}}$) reflect the preference of the anion X^- relative to the Cl^- ion observed for each electrode. Interestingly, these improved electrodes provided the highest degree of selectivity for the SCN^- ion. For example, the SCN^- ion is 630 times favorable than the Cl^- ion for the electrode modified with $^n\mathrm{Bu_2SnIH}$. When the selectivity of the electrodes differs from the Hofmeister lyotropic anion selectivity sequence, the selectivity is generally not governed by simple anion lipophilicity but by specific chemical interaction between the neutral carriers and anions.[5] Therefore, organotin compounds, which were fixed in PVC membranes, are considered to exhibit the strongest interaction with the SCN^- ion among a series of common monovalent anions.

No marked influence of the electronegative substituents Y on the selectivities for anions of the electrodes based on trialkyltin halide ($\mathrm{R_3SnY}$) has been reported.[6] However, in this study, remarkable influence was observed by the difference between electronegative substituents Y of $^n\mathrm{Bu_2SnYH}$ (Y = F, Cl, I, OMe). For example, the electrodes improved by $^n\mathrm{Bu_2SnClH}$ and $^n\mathrm{Bu_2SnIH}$ displayed the following selectivity pattern:

$$\mathrm{SCN^-}\,(\log k^{\mathrm{Pot}}_{\mathrm{Cl,X}} = 2.1) > \mathrm{ClO_4^-}\,(0.6) > \mathrm{I^-}\,(0.4) > \mathrm{AcO^-}\,(0.2) > \mathrm{Br^-}\,(0.2) > \mathrm{NO_3^-}\,(0.1) > \mathrm{Cl^-}\ \text{for}\ {}^n\mathrm{Bu_2SnClH}$$

$$\mathrm{SCN^-}\,(\log k^{\mathrm{Pot}}_{\mathrm{Cl,X}} = 2.8) > \mathrm{I^-}\,(1.0) > \mathrm{ClO_4^-}\,(0.8) > \mathrm{NO_3^-}\,(0.4) > \mathrm{Br^-}\,(0.1) > \mathrm{Cl^-} > \mathrm{AcO^-}\,(-0.8)\ \text{for}\ {}^n\mathrm{Bu_2SnIH}$$

Such influence of the electronegative substituents Y on the selectivities has been found for the electrodes based on dibutyltin dihalides ($^n\mathrm{Bu_2SnY_2}$).[21] Furthermore, the distinct electronegative substituents Y led to the difference in the degree of selectivity for the SCN^- ion. The degree of selectivity for the SCN^- ion of the electrode improved by $^n\mathrm{Bu_2SnIH}$ ($\log k^{\mathrm{Pot}}_{\mathrm{Cl,SCN}} = 2.8$) was about eight times higher than that of the electrode improved by $^n\mathrm{Bu_2SnFH}$ ($\log k^{\mathrm{Pot}}_{\mathrm{Cl,SCN}} = 1.9$).

In conclusion, novel electrodes using the PVC liquid membranes with fixed organotin compounds was developed by the reaction of PVC with di-*n*-butyltin halide hydrides $^n\mathrm{Bu_2SnYH}$. The fixation of organotin compounds in PVC membranes is likely to prevent the effusion of organotin compounds as neutral carriers, resulting in good potential stability. These electrodes were found to exhibit non-Hofmeister selectivity patterns, and provided the highest degree of selectivity for the SCN^- ion.

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