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Thiocyanate Solvent Polymeric Membrane Ion-selective Electrode Based on Cobalt(III) α,β,γ,δ-Tetraphenylporphyrin Anion Carrier

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A solvent polymeric membrane ion-selective electrode based on thiocyanato(α,β,γ,δ-tetraphenylporphynate)cobalt(III) was developed. The electrode membrane exhibits $SCN^- >> I^- > NO_2^- >> ClO_4^- > HCO_3^- > HPO_4^{2-} > Cl^- \approx Br^- > NO_3^- \approx SO_4^{2-}$ selectivity sequence with a preference for SCN^- over ClO_4^- by $10^{2.5} - 10^{3.1}$. Response of the electrode is linear in the 10^{-5} to 10^{-1} M concentration range for SCN^- with a slope of -49 ± 2 mV/log a.

In anion-selective liquid membrane electrodes based on classical ion exchangers, the selectivity is governed by the free energy of transfer of anions from aqueous solutions to the membrane phase and consequently by the hydration energy. Therefore, electrodes of this kind exhibit roughly the same selectivity pattern as the so-called Hofmeister lyotropic series. It was shown that certain transition metal complexes which interact with specific anions are able to induce the selectivity deviated from the selectivity pattern of electrode membranes containing classical ion exchangers. Thus, the development of anion carrier-based electrodes has become of interest in recent years. Although several authors have reported anion-selective electrodes based on positively charged anion carriers such as cobalt(III) or manganese(III) complexes of porphyrins and vitamin B_{12} derivatives, they have not paid much attention to counter ions of the carriers in preparations of electrode membranes.1-3) It seems to be more adequate that electrode membranes are prepared by using a salt of a carrier cation with a primary ion, since conversion of a counter ion of the carrier to a more preferred anion is expected to increase affinity of the carrier to the membrane phase. On the basis of this expectation, we have developed a thiocyanate ion-selective electrode of an anion carrier type without use of highly alkylated porphyrins.2) A sensing material based on thiocyanate salt of cobalt(III) complex of α,β,γ,δ-tetraphenylporphyrin (TPP) described in the present communication showed sufficiently high performances and selectivity for use in a thiocyanate ion-selective electrode.

Poly(vinylchloride) (PVC, $\overline{MW}$ = 1100) was purchased from Katayama Chem. A plasticizer, 2-nitrophenyloctylether (o-NPOE), and TPP were from Dojin Chemical Laboratory (Kumamoto, Japan). Other usual reagents were of reagent grade.

Distilled and subsequently deionized water was used throughout. The sensing material, i.e., thiocyanate salt of Co(III)-TPP was prepared as follows: first, Co(II) complex of TPP was prepared by the method of Adler et al.4) and then Co(III)-TPP-Cl was obtained as described.5) The resulting chloride salt of the complex was converted into thiocyanate salt by shaking ca. 100 mg of the chloride salt dissolved in 100 ml of chlroform with 100 ml of 1 M (M = mol/dm^3) NaSCN on a mechanical shaker. This step was repeated three times and then the organic phase was washed several times with water. Chloroform was evaporated to ca. 20 ml on a rotary evaporator. The rest of the solvent was evaporated in air. The resulting crystals were recrystallized from chloroform-methanol mixture and dried in a vacuum desiccator. The final product thus obtained was identified by means of TLC and CHN analyses. Membranes containing 1, 2 or 3% of the complex, 30% of PVC and 67 to 69% of o-NPOE were prepared according to the reported method.6) Small pieces of the membranes were glued to tips of an electrode body supplied from Denki Kagaku Keiki Co. (Tokyo, Japan). After the tips were filled with an internal solution (0.01 M NaCl, 0.01 M NaSCN), the electrode was assembled. In electromotive force (EMF) measurements, an Ion-meter IOC-10 (Denki Kagaku Keiki Co.) and a double junction saturated calomel electrode with a 0.1 M lithium acetate salt bridge solution were used. Selectivity coefficients were determined by the separate solution method in which 0.1 M solutions of sodium salts of appropriate anions were used. For perchlorate, the selectivity coefficient was also determined by the mixed solution method. Here, the concentration of perchlorate was fixed at 0.1 M and that of the primary ion was varied. In evaluation of pH effect on electrode responses, pH of 0.001, 0.01 and 0.1 M NaSCN solutions initially adjusted to about 4 by addition of 0.1 M HCl was gradually increased by addition of NaOH solutions (0.01 - 1 M) up to 12.

First, membranes containing chloride salt of the complex were prepared and their performances were examined. During storage of the membranes both in water and air, the chloride salt of the complex tended to crystallize within the membranes or on their surfaces resulting on deterioration in slopes of calibration curves as well as selectivity. On the other hand, no visible change was observed in the case of membranes containing thiocyanate salt of the complex. This means that affinity of the positively charged carrier to the membrane can be enhanced by replacement of its counter ion from less preferred chloride to more preferred thiocyanate. The presented method is a more simple approach in order to increase the affinity of the carrier complex cation to the membrane phase (more exactly to the plasticizer), compared with introduction of bulky organic residues to porphyrin ligands.2)

EMF response of the electrode based on a membrane containing 3% of Co(III)-TPP-SCN is shown in Fig. 1. The response is linear for unbuffered solutions of NaSCN in the range 10^{-5} - 10^{-1} M (curve 1). Curve 2 is a response of the electrode for solutions in the presence of a fixed amount of perchlorate 0.1 M. The curve gives -2.5 as a value of the selectivity coefficient for thiocyanate over perchlorate in logarithmic unit. The slope of electrode calibrations decreased from an initial -55 mV/log a for freshly prepared electrode to -49 ± 2 mV/log a over a period of several weeks.

Comparison of selectivity coefficients obtained by the separate solution method for Co(III)-TPP-SCN and a classical ion exchanger (Capriquat) is shown in Fig. 2. In spite of proposing the electrode itself for use in a thiocyanate ion-selective electrode, selectivity coefficients for all anions were related to chloride ion. This was done for the sake of comparison with similar works.[1,2] Figure 2 clearly shows that while for the classical ion exchanger selectivity for ClO_4^- is 1.3 orders higher than that for SCN^-, for the anion carrier membrane selectivity for SCN^- is 2.7 orders higher than that for ClO_4^-. Therefore, overall change in selectivity induced by specific interaction with the complex is four orders.

Virtually no pH dependence was observed with the electrode having the membrane containing 3% of the sensing material in the pH range from 5 to 11 (Fig. 3). Slight pH dependence was observed in the case of membranes containing less than 2% of the complex in both strongly acidic or alkaline region at lower levels of the primary ion (0.001 and 0.01 M). However, after overnight soaking in 0.1 M $NaNO_2$ potentials become pH dependent with a slope of 10 mV/log a and also some deteriorations of slopes in electrode calibrations occur. This is agreement with our previous studies on behavior of electrode membranes containing Co(III)-TPP complex in nitrite form. We have no clear explanation for this behavior yet, but we are considering the possibility that in the case of nitrite salt of the complex, real concentrations of anionic active sites in the

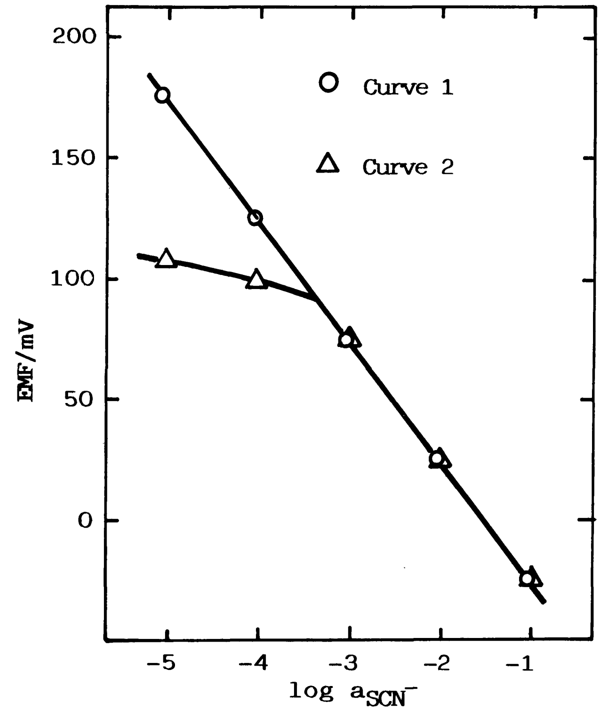

Fig. 1. Response of electrode membrane containing 3% of Co(III)-TPP-SCN in unbuffered NaSCN solutions (○), and in solutions in the presence of 0.1 M interfering ion ClO_4^- (△).

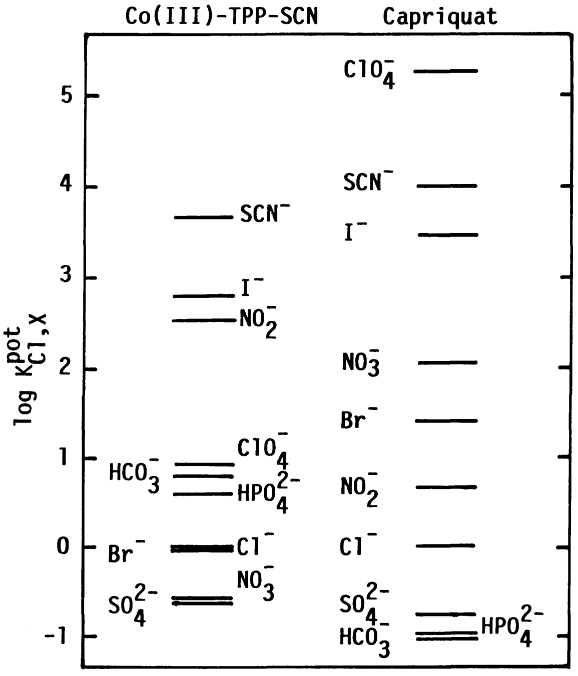

Fig. 2. Selectivity coefficients determined by the separate solution method for membrane containing Co(III)-TPP-SCN compared to those of classical ion exchanger (Capriquat).

membrane are very low due to the exceptionally strong interaction of nitrite with the central colbalt(III) in the complex so that charged sites present in the membrane as impurities from PVC and/or the plasticizer can compete with anionic function of the electrode membrane and the electrode starts to act as a H^+ electrode to some extents. Further investigation of this important phenomenon is in full progress.

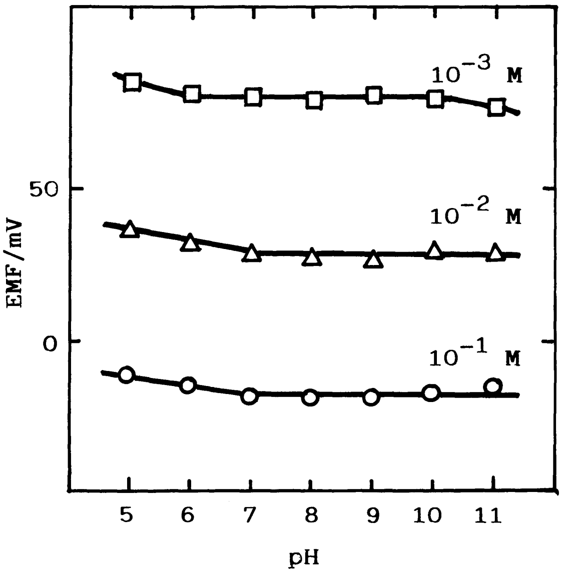

Fig. 3. Dependence of EMF on pH for electrode having membrane containing 3% of Co(III)-TPP-SCN in 10^{-3} to 10^{-1} M NaSCN solutions.

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