2454 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2454—2456 (1973) [Vol. 46, No. 8

The Liquid Membranes of the Thiocyanate Ion-Sensitive Electrode

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(Received January 29, 1973)

Ion-selective electrode membranes responsive to the thiocyanate ion were prepared by using ion-association extraction systems. A crystal violet or tetraphenylarsonium cation was used as an ion exchange-site in the liquid nitrobenzene membrane. The liquid membrane electrcde exhibits an ideal Nernstian response to the thiocyanate ion down to 10^{-5} M. The selectivity of the liquid membrane largely depends on the extractability of the diverse anion into nitrobenzene. The order of the selectivity coefficients, K_j, is as follows:

$$ClO_4^- > IO_4^- > SCN^- > I^- > ClO_3^- > NO_3^- > Br^- > BrO_3^- > Cl^-$$

High selectivities for thiocyanate over SO_4^{2-}, $H_2PO_4^-$, Cl^-, BrO_3^-, and Br^- were observed. The membrane potential is independent of the pH variation in the region from pH 2 to 12.

In recent years many kinds of selective ion-sensitive electrodes have been developed as analytical sensors which are capable of determining the activities of objective ions selectively.

Commercial thiocyanate-sensitive electrodes are usually prepared by using a compacted polycrystalline membrane of silver thiocyanate or a mixture of it with silver sulfide. A bromide-sensitive electrode with a AgBr membrane was also used as a thiocyanate-sensitive electrade,[1] since the thiocyanate ion reacts with a AgBr membrane to form a thin film of insoluble AgSCN on the membrane surface.

Hirsh and Protoch have found that the perchlorate ion-selective electrode of the liquid-membrane type is sensitive to perrhenate and thiocyanate ions; they performed the titration of thiocyanate with mercuric nitrate using this perchlorate ion-selective electrode.[2]

In this work, the thiocyanate-sensitive liquid membranes were prepared by using ion-association extraction systems, and the performance of the liquid membranes was studied.

Experimental

Apparatus and Chemicals. The measurements of the membrane potential were made with a Takeda Riken electrometer, TR-8651. The conductance of the liquid membrane was measured at 25 °C by the use of a Yanagimoto conductivity outfit, MY-7. The crystal violet and tetraphenylarsonium chloride were obtained from the Kishida Kagaku Co. and Wako Pure Chemicals Co. respectively. The thiocyanate stock solution was prepared by dissolving reagent-grade sodium thiocyanate in deionized water and was then standardized titrimetrically by the Volhard method. This stock solution was diluted to the desired concentration.

Preparation of the Liquid Membrane. Both the crystal violet and the tetraphenylarsonium ion were used as anion-exchange sites. By such a large, singly-charged cation, the thiocyanate ion can be extracted into nitrobenzene. The crystal-violet membrane was prepared by extraction with crystal-violet dyestuff in the following manner.

One hundred ml of a 1×10^{-3} M sodium thiocyanate solution and 100 ml of an equimolar crystal-violet solution were transferred into a separating funnel. The resulting aqueous solution was shaken with 100 ml of nitrobenzene for 60 min. The organic phase which was thus separated from the aqueous phase was shaken again with 100 ml of the 1×10^{-3} M sodium thiocyanate solution in order to purify it. After the phase separation had been completed, the organic solution was filtered through a dry filter paper in order to remove droplets of water; it was then diluted to 1×10^{-4} M with nitrobenzene when used as a thiocyanate-sensitive liquid membrane.

The thiocyanate ion was precipitated as white needles from an aqueous solution using the tetraphenylarsonium ion. The tetraphenylarsonium membrane was prepared by dissolving the precipitate in nitrobenzene.

Measurement of the Liquid Membrane Potential. The electromotive force of the following concentration cell was measured by means of the electrometer in order to evaluate the membrane performance:

$$+ \ \underbrace{\text{SCE/Reference solution/organic liquid membrane/}}_{\text{(Electrode)}}\ \text{Sample solution/SCE} \ -$$

The cell assembly was the same as that described elsewhere.[3] The reference solution and the sample solution were separated in the lower part of a U-shaped glass tube by the use of a liquid membrane such as a nitrobenzene solution of tetraphenylarsonium thiocyanate.

Results and Discussion

Membrane Potential. Figure 1 shows the effect of the concentration of the membrane solute on the membrane potential. An increase in the concentration

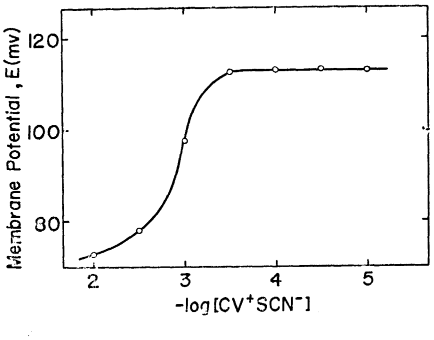

Fig. 1. Effect of membrane site concentration (15 °C).
Reference solution: 1×10^{-3} M NaSCN
Sample solution: 1×10^{-5} M NaSCN
CV+: Crystal violet

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[1] R. A. Durst (Editor), *Ion-selective electrodes*, N. B. S. Spec. Publ. 384, U. S. Printing office, Washington (1970).

[2] R. F. Hirsch and J. D. Protoch, *Anal. Lett.*, **2**, 295 (1969).

[3] N. Ishibashi and H. Kohara, *ibid.*, **4**, 785 (1971).

of the membrane solute beyond about $10^{-3.5}$ M causes a drop in the membrane potential. This is probably due to the elution of the membrane solute on an adjacent aqueous solution. Hence, a dilute organic solution is preferable as the liquid membrane. However, the electrical resistance of the membrane increases with a decrease in the concentration of the membrane solute, and the membrane potential tends to become unstable. Consequently, 1×10^{-4} M was used as the membrane concentration throughout the study.

The membrane potential can be expressed by the following equation:

$$E = (RT/F) \ln (a'_{\mathrm{SCN}}/a''_{\mathrm{SCN}}) \quad (1)$$

where a'_{SCN} and a''_{SCN} denote the thiocyante activities of the reference solution and the sample solution respectively. As the reference solution, we used a 1×10^{-3} M aqueous sodium thiocyante solution. Fig. 2 shows the electrode response to the sample solution at varying concentrations; the figure shows that an ideal Nernstian relationship of the potential against the logarithmic activity of the thiocyanate ion holds down to 10^{-5} M of the sodium thiocyanate solution. No difference was found in the linearity range of the electrode responses between the crystal-violet membrane and the tetraphenylarsonium membrane.

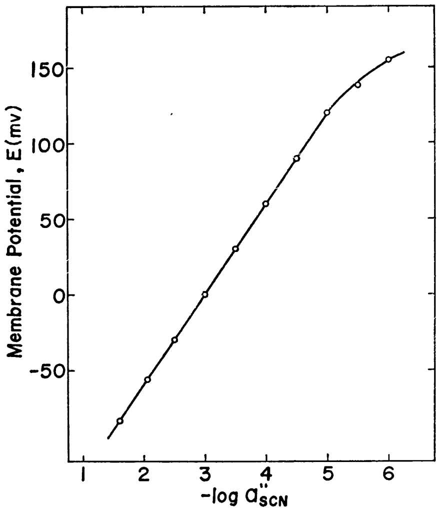

Fig. 2. Electrode response to aqueous NaSCN solution (26°C).
Reference solution: 1×10^{-3} M NaSCN
Membrane solvent: Nitrobenzene

Electrode Response as a Function of the pH. The pH effect on the membrane potential is given in Fig. 3. The pH adjustment was made by the addition of sodium hydroxide or sulfuric acid. The variation in pH has no effect on the membrane potential over the range from pH 2.5 to 12. The crystal-violet membrane showed a somewhat larger decrease of the membrane potential below pH 2 than did the tetraphenylarsonium membrane. The potential decrease in the crystal-violet membrane electrode below pH 2 may be attributed to the conversion of the crystal-violet to its acidic form and to the change in the liquid-junction potential between an agar salt bridge and the sample solution.

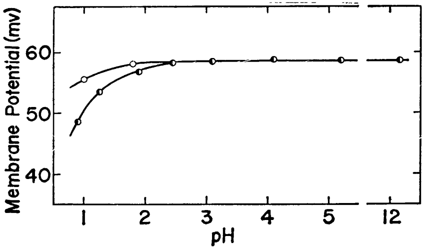

Fig. 3. Electrode response as a function of pH (15°C).
Reference solution: 1×10^{-3} M NaSCN
Sample solution: 1×10^{-4} NaSCN
-○- Tetraphenylarsonium membrane
-◐- Crystal violet membrane

The tetraphenylarsonium membrane is affected only by the variation in the liquid-junction potential.

Electrode Response in the Presence of Diverse Anions. The electrode response in the presence of an interfering ion is empirically given by the following equation[4]:

$$E = \text{constant} - 2.303\,RT/F \log (a''_{\mathrm{SCN}} + K_j(a_j'')^{1/z}) \quad (2)$$

where K_j is the selectivity coefficient of j-ion for the thiocyante electrode and where z is the charge of the j-ion. As can be seen from Fig. 4, the electrode potential is depressed by the presence of diverse ions. A large value of K_j corresponds to a remarkable change in the membrane potential.

The selectivity coefficients can be obtained by the measurement of the membrane potentials in both the presence and absence of diverse ions. The observed values of K_j are listed in Table 1 with respect to the crystal-violet membrane. From the K_j values, the order of interference is found to be:

$ClO_4^- > IO_4^- > I^- > ClO_3^- > NO_3^- > Br^- > BrO_3^- > Cl^-$, $H_2PO_4^-$, $CH_3CO_2^-$, SO_4^{2-}

The tetraphenylarsonium membrane gave the same selectivity coefficient, K_j. It can be said that the se-

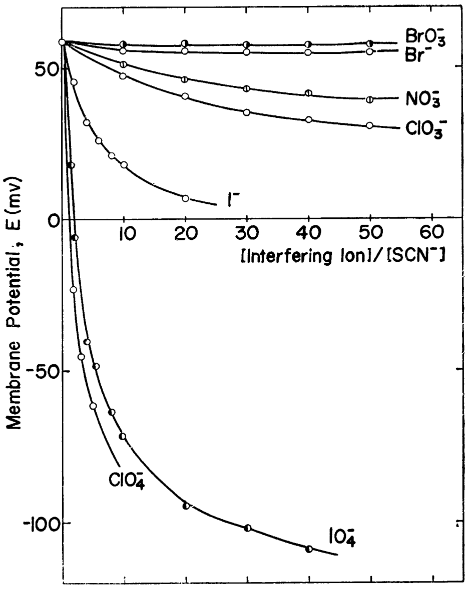

Fig. 4. Electrode response in the presence of interfering anion.

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[4] J. W. Ross, *Science*, **156**, 1378 (1967).

TABLE 1. SELECTIVITY COEFFICIENTS OF THIOCYANATE-SENSITIVE LIQUID MEMBRANE ELECTRODE (EXCHANGE-SITE: CRYSTAL VIOLET)

Anion	K_j	Anions	K_j
ClO_4^-	12.0	Br^-	0.006
IO_4^-	6.7	BrO_3^-	0.002
SCN^-	1.0	Cl^-	$<10^{-4}$
I^-	0.34	$H_2PO_4^-$	$<10^{-4}$
ClO_3^-	0.05	$CH_3CO_2^-$	$<10^{-4}$
NO_3^-	0.03	SO_4^{2-}	$<10^{-4}$

quence of selectivity is independent of the site species in nitrobenzene. The electrode has higher selectivities for the thiocyanate ion over bromide and chloride ions than does the solid-state electrode.¹⁾ From the conductivity measurement of the liquid membrane, it was found that the site and its counter anion in nitrobenzene were in an almost complete dissociation.

According to Eisenman's theoretical treatment⁵⁾ of the membrane potential, the selectivity of the electrode with a liquid membrane is determined by the relative partition coefficient and the mobilities between the objective ion and the competitive ion in a limiting case of a complete dissociation. The sequence of K_j values in Table 1 is consistent with the ease of the extraction of the anions into the organic solvent.⁶⁾ Hence, the observed selectivity order qualitatively supports Eisenman's theoretical prediction, since there is no large difference among the ionic mobilities.

The authors wish to thank the Ministry of Education for its grant-in-aid.

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5) F. Conti and G. Eisenman, *Biophys. J.*, **6**, 227 (1966).

6) N. A. Gibson and D. C. Weatherburn, *Anal. Chim. Acta*, **58**, 159 (1972).