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SOME ION-SELECTIVE ELECTRODES BASED ON ION ASSOCIATE IMPREGNATED IN PLASTICS MATRIX

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Perchlorate, thiocyanate, 1-naphthalenesulfonate, hydrogenphthalate and salicylate ion-selective electrodes with polyvinyl chloride membranes containing the ion associate and plasticizer were prepared. The electrodes showed a Nernstian response and had high selectivities for the objective anions in the presence of acetate, bromide or chloride.

An ion-selective electrode of the liquid membrane type seems to be somewhat troublesome in its manipulation, compared to an electrode of the solid membrane type. The virulence of the organic solvent of the liquid membrane is undesirable in practical use. We are preparing the plastics electrode membrane in which an active material of the liquid membrane is impregnated. This letter describes the preparation and analytical behavior of the ion-selective electrode with a polyvinyl chloride (PVC) membrane incorporating the ion associate of a high molecular weight ammonium ion with the objective anion, such as perchlorate, thiocyanate, 1-naphthalenesulfonate, hydrogenphthalate or salicylate. Thomas et al. have prepared the calcium and nitrate ion-selective electrodes with PVC membrane.[1-3] Freiser et al. have developed the platinum wire electrodes coated with PVC film.[4,5] In this study, dioctyl phthalate (DOP) was used to obtain the PVC membrane of moderate hardness, though a particular plasticizer was not contained in Thomas' membrane and Freiser's electrode film.

Tetradecyldimethylbenzylammonium or methyltricaprylylammonium ion was used as an anion exchange site in the membrane. The PVC membrane was prepared by the following procedure. The PVC solution in an appropriate organic solvent, the plasticizer (DOP) and the ion associate, i. e., the ammonium salt of the objective anion, were mixed at

Table 1 Composition of PVC Electrode Membrane

Electrode	Anion Exchange Site	Weight Ratio of Membrane Component PVC Soln.		DOP		Ammonium Salt
ClO_4^-	Tetradecyldimethylbenzylammonium Ion	5.0[a]	:	1.0[c]	:	1.0[e]
SCN^-		5.0[a]	:	1.0[c]	:	1.0[e]
1-Naphthalenesulfonate	Methyltricaprylylammonium Ion (Aliquat 336 S)	3.5[b]	:	0.0	:	1.0[f]
Hydrogenphthalate		2.5[b]	:	1.0[d]	:	1.0[f]
Salicylate		4.0[b]	:	2.0[d]	:	1.0[f]

a) added as cyclohexanone solution (10 % w/w).
b) added as tetrahydrofuran solution (20 % w/w).
c) di(2-ethylhexyl)ester.
d) di(n-hexyl)ester.
e) added as white powder salt.
f) added as 1,2-dichloroethane solution.

the weight ratios as shown in Table 1. The mixture was spread on a glass sheet and left more than 48 hr in order to evaporate the solvent. A white or transparent membrane 0.5 - 1 mm thick was obtained. A 5 - 10 mm diameter membrane was affixed to a glass tube or an Orion electrode body. The following electrochemical cell was assembled to examine the response of the membrane.

+ Ag-AgCl or SCE/ Reference Soln./ Membrane/ Sample Soln./ SCE -
↑————Ion-selective Electrode————↑

The electromotive force of the cell was measured by using a Takeda Riken Electrometer TR 8651. The selectivity coefficient was determined by the mixed solution method.[1)]

The performances of the electrodes are summarized in Table 2. The electrodes showed a linear response down to 10^{-3} - 10^{-4} M, with a nearly Nernstian slope of 55 - 59 mV per activity decade at room temperature. It was recognized that the lower limit of a linear response of the hydrogenphthalate electrode was extended to 10^{-4} M by decreasing the content of the ion associate in its PVC membrane. The detailed study of the dependence of the sensitivity on the content of the ion associate in the membrane is in progress. The selectivity of the PVC membrane electrode was comparable to that of the liquid membrane electrode prepared by using 1,2-dichloroethane as the solvent of the membrane. The electrodes had high selectivities for the objective anions in the presence of acetate, bromide or chloride. The response time varied with the concentration of sample solutions. In the concentration range higher than 10^{-3} M of an objective ion, equilibrium potentials were achieved within 1 min. Several minutes or a longer time, however, was required below 10^{-3} M.

Table 2 Performances of PVC Membrane Electrodes

Electrode	Slope (mV/ log a)	Lower Limit of Linear Response(M)	Selectivity Coefficient (log K)
ClO_4^-	-55	$10^{-4.0}$	Br^- <-3.0, NO_3^- -2.9, I^- -2.0, SCN^- -1.7,
SCN^-	-59	$10^{-3.5}$	Br^- -1.2, NO_3^- -1.1,
1-Naphthalenesulfonate	-58	$10^{-3.5}$	Cl^- -2.9, Br^- -1.9, CH_3COO^- <-3.0, Benzenesulfonate -1.5,
Hydrogenphthalate[a]	-59	$10^{-3.0}$	Cl^- -2.6, NO_3^- -1.3, iso-Phthalate -3.0,
Salicylate	-59	$10^{-3.0}$	Cl^- -2.3, NO_3^- -0.8, CH_3COO^- <-3.0, SO_4^{2-} <-3.0,

a) pH of sample solution was maintained at 4.0

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References

1) G.J. Moody, R.B. Oke, and J.D.R. Thomas, Analyst, 95, 910 (1970).
2) J.E.W. Davies, G.J. Moody, and J.D.R. Thomas, Analyst, 97, 87 (1972).
3) G.H. Griffiths, G.J. Moody, and J.D.R. Thomas, Analyst, 97, 420 (1972).
4) R.W. Cattrall, and H. Freiser, Anal. Chem., 43, 1905 (1971).
5) H. James, G. Garmack, and H. Freiser, Anal. Chem., 44, 856 (1972).

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