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An Evaluation of Ion-exchange Membrane Electrodes

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Synopsis. The potentiometric response behavior and selectivity characteristics of ion-exchange membrane electrodes have been investigated. Nernstian responses were obtained for inorganic anions such as perchlorate, nitrate, and chloride with each form of Selemion ASV membrane. Highly selective exclusions of the divalent sulfate and large organic sulfonate anions were observed with those membranes.

There have been many reports on the use of ion-exchange resins as heterogeneous resin membranes, which were made of ion-exchange resins embedded into high polymer or silicone rubber binders.[1-3] The electrodes of these types, however, have not shown good selectivity among individual ions and have been of little utility. Recently, a hydrophobic anion-exchange resin electrode having a wide selectivity range has been developed by Jyo *et al.*[4] On the other hand, a homogeneous ion-exchange membrane has never been successfully used as an ion-sensing material. Birch and Clarke have reported on a surfactant selective electrode with an Asahi anion-exchange membrane, which showed only a poor response to surfactant anions.[5]

In this paper, the authors examined commercially available ion-exchange membranes as ion-sensing materials and found that these membranes showed linear and quick responses for inorganic univalent anions, such as perchlorate, nitrate, and chloride over the concentration range from 10^{-1} M (1 M=1 mol dm^{-3}) to nearly 10^{-4} M. These membranes exhibited a highly selective exclusion of the divalent sulfate and large organic anions such as *p*-toluenesulfonate (TsO$^-$) and benzenesulfonate (PhSO$_3^-$), in contrast to liquid membrane electrodes. The differences of the selectivity characteristics among these membranes were discussed qualitatively on the basis of their membrane structures.

Experimental

Reagents. The ion-exchange membranes used were Selemion ASV, AMV, and DMV produced by the Asahi Glass Co. Ltd. AMV is an anion permselective membrane for the use of electrodialysis, having an ion-exchange site of -N(CH$_3$)$_3^+$. ASV is a univalent anion permselective membrane having not only a functional group similar to AMV but also a cation exchange site, which can effectively repel polyvalent anions.[6] DMV is an anion permselective membrane for use in diffusion dialysis, having functional groups of -NH$_3^+$ and $\rangle$NH$_2^+$. Cations, except proton and nondissociative organic molecules cannot pass through a DMV membrane. The substrates of these membranes are made of polystyrene–butadiene copolymer.[6] The ClO$_4^-$, NO$_3^-$, and TsO$^-$ forms of these membranes were made by soaking their original chloride forms in an aqueous solution of a sodium salt of the objective anion. The air-dried chloride form of ASV has been soaked in 1-decanol or nitrobenzene for 3 d in order to examine the effects of the impregnated solvents on membrane selectivity. Sodium hydroxide and *p*-toluene-sulfonic acid were used to control the pH of the sample solution.

Apparatus. A membrane electrode of the double junction type with an outer filling solution of 0.1 M sodium salt of each anion was used. The electrode potentials were measured by an Orion Digital Ionalyzer Model 601 connected to a Matsushita Penrecorder Model VP654A. All measurements were carried out by stirring at 25±0.5 °C.

Results and Discussion

The potentiometric response characteristics of ClO$_4^-$, NO$_3^-$, Cl$^-$, and TsO$^-$ forms of ASV and DMV membranes with respect to the sensitivity, slope of the calibration curve, and response time are summarized in Table 1. Each value listed in the table is a mean value of four independent measurements. The ΔE_{1-4} denotes the potential difference between the solutions of 10^{-1} M and 10^{-4} M, which was used as an index of sensitivity. The slopes were estimated by a regression analysis in the concentration range of from 10^{-1} M to 10^{-3} M. The response time was defined as a period of time when the electrode was dipped until the membrane potential reached a steady value within ±0.5 mV, and was listed as a mean value obtained from 10^{-1} M to 10^{-4} M.

TABLE 1. POTENTIOMETRIC RESPONSE BEHAVIOR OF ION-EXCHANGE MEMBRANE ELECTRODES

Membrane and form	ΔE_{1-4} / mV	Slope / mV/pa	Response time / min
ASV : ClO$_4^-$	174±3.5	59.8	0.87
DMV : ClO$_4^-$	160±5.2	58.6	1.4
ASV : NO$_3^-$	168±3.0	60.1	0.54
DMV : NO$_3^-$	159±2.0	59.9	0.82
ASV : Cl$^-$	162±2.4	60.2	0.78
DMV : Cl$^-$	154±3.7	59.1	0.89
ASV : TsO$^-$	148±6.1	55.9	4.2
DMV : TsO$^-$	168±4.6	61.0	0.73

Each form of ASV and DMV, except the TsO$^-$ form of ASV, gave the Nernstian response over the concentration range of from 10^{-1} M to nearly 10^{-4} M, and considerably quick response at concentrations above 10^{-3} M. ASV was superior to DMV in sensisivity for the inorganic univalent anions, while DMV showed a better response to TsO$^-$ than ASV did. The TsO$^-$ form of ASV gave a poor response in both sensitivity and response time. This phenomenon was attributed not only to the repulsion between the surface cation exchange layer and an organic sulfonate anion but also to the steric hindrance between the ASV membrane and a large organic anion. The response characteristics of AMV were almost the same as those of DMV.

Table 2 summarizes the selectivity characteristics of these membranes. The selectivity coefficients, log $K^{\mathrm{pot}}_{\mathrm{i\text{-}j}}$ of the ClO$_4^-$, NO$_3^-$, Cl$^-$, and TsO$^-$ forms of ASV and DMV were measured by the separate solution

TABLE 2. SELECTIVITY COEFFICIENTS, log K^{pot}_{i-j} OF ION-EXCHANGE MEMBRANE ELECTRODES

Membrane and form (Sensing anion, *i*)	Interfering anion, *j*					
	ClO_4^-	NO_3^-	Cl^-	$PhSO_3^-$	TsO^-	SO_4^{2-}
ASV : ClO_4^-	0	−0.72	−1.40	−2.11	−2.21	−3.00
DMV : ClO_4^-	0	−0.38	−0.60	−0.73	−0.80	−1.40
ASV : NO_3^-	0.60	0	−0.28	−1.28	−1.70	−1.53
DMV : NO_3^-	0.28	0	−0.10	−0.33	−0.37	−0.46
ASV : Cl^-	1.11	0.27	0	−0.85	−1.35	−1.09
DMV : Cl^-	0.37	0.05	0	−0.25	−0.30	−0.47
ASV : TsO^-	1.48	0.95	0.48	0.05	0	−1.02
DMV : TsO^-	0.87	0.48	0.25	0.03	0	−0.58

Concn of interfering anion; 10^{-2}M

method. The reproducibility of the value was within ±0.08.

The order of the magnitude of the selectivity coefficients among the univalent anions was $ClO_4^- > NO_3^- > Cl^- > PhSO_3^- > TsO^-$. This sequence of interference was different from the results reported with the liquid membrane electrodes of *o*-dichlorobenzene, *i.e.*, $ClO_4^- > TsO^- > PhSO_3^- > NO_3^- > Cl^-$.[7] It was found that organic anions, such as $PhSO_3^-$ or TsO^-, caused less interference with the ion-exchange membranes than with the liquid membranes. However, the sequence of the interference among the inorganic anions was similar to that of the liquid membrane. ASV suffered less from the interference of a divalent sulfate anion than DMV owing to its univalent permselectivity. The selectivity characteristics of these membranes were examined more extensively with their chloride forms, as shown in Fig. 1. The selectivity range was widest in ASV and decreased in the order of ASV≫AMV>DMV. From the results, the degree of quaternization of the ion-exchange site seems to exert a smaller effect on the selectivity range than the presence of the surface cation-exchange site. Almost all organic anions tested caused less interference with these membranes than the inorganic anions. This result may be attributed to the difficulty in diffusion of the large organic anions into these compact membranes owing to their strong interaction with the high polymer chains.

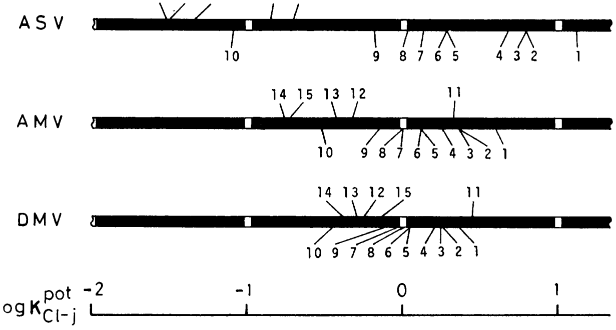

Fig. 1. Selectivity coefficient diagrams of Cl^- form ion-exchange membranes.
Interfering anion: (1) ClO_4^-, (2) BF_4^-, (3) SCN^-, (4) I^-, (5) NO_3^-, (6) Br^-, (7) ClO_3^-, (8) NO_2^-, (9) BrO_3^-, (10) SO_4^{2-}. (11) $C_8H_{17}OSO_3^-$ (octyl sulfate), (12) $PhSO_3^-$ (benzenesulfonate), (13) TsO^- (*p*-toluenesulfonate), (14) $C_8H_{17}SO_3^-$ (1-octanesulfonate), (15) 1-naphthalenesulfonate.

The effect of pH of the sample solution on the membrane potentials of the ClO_4^- forms of these membranes was examined. ASV sustained a constant potential over a wide pH range from 5.0 to 11.0, whereas DMV did so only in the range of from pH 6.0 to 9.0. This difference in the accessible pH range between ASV nad DMV is due to the degree of quaternization of their ion-exchange sites.

It has been reported by Jyo *et al.* that the selectivity range of the liquid membrane electrodes were influenced more by the membrane solvents than the ion-exchange sites.[8] The selectivity coefficients of the Cl^- form of ASV, however, were affected little by the impregnation of the membrane with 1-decanol. Nitrobenzene seemed to damage the high polymer chains of ASV.

In conclusion, though the ion-exchange membranes did not show a special advantage in sensitivity and in selectivity, in a conventional sense, over the liquid membranes, they did seem to have the following advantages: A high polymer membrane is very strong mechanically and has a very long life time. And in particular, a high polymer membrane has the possibility of making its selectivity highly specific for a certain ion by introducing a particular functional group into the high polymer chains, just as ASV showed a specific repulsion to divalent sulfate by its surface cation-exchange site, or to large organic sulfonate anions owing to their strong interaction with the high polymer chains.

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