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A NEW TYPE OF AN ION-SELECTIVE ELECTRODE BASED ON AN ANION EXCHANGE RESIN WITH A HYDROPHOBIC SITE

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A new type of an anion-selective electrode has been developed. The sensitive membrane of the electrode is an anion exchange resin impregnated with nitrobenzene. The exchange site of the anion exchange resin is a hydrophobic quaternary ammonium group with a long alkyl chain. The performance of the electrode was comparable to that of usual or commercial liquid anion exchanger membrane electrodes.

In this communication, we present a new type of an ion-selective electrode. The sensitive membrane of the electrode is a hydrophobic anion exchange resin impregnated with nitrobenzene. The exchange site of the anion exchange resin is a hydrophobic quaternary ammonium group with a long alkyl chain and resembles to sites of liquid anion exchangers.

The anion exchange resin was prepared by the chloromethylation of Amberlite XAD-2 (diameter, ca. 0.5 mm), a crosslinked styrene-divinylbenzene copolymer of a macroreticular type, and the subsequent quaternization of the chloromethylated resin with dimethyltetradecylamine. The resulting resin was repeatedly washed with benzene and ethanol to eliminate the amine unreacted. After the resin was conditioned with 1 M (M = mol dm^{-3}) HCl and 1 M NaOH, alternately, the resin was obtained as the chloride form having the capacity of 0.4 -0.6 meq g^{-1}. Conversion of the resin form from the chloride form to the chlorate, nitrate or perchlorate form was accomplished by ion exchange in a column. An aqueous solution of an appropriate sodium salt (1 M, 100 - 200 ml) was passed through the column containing the resin of the chloride form (1 - 2 g) at the rate of a few drops per minute. The resin was washed in the column with ethanol or water, and dried in a vacuum desiccator. One particle of the resin thus treated was fixed to one end of a teflon tube (i.d. 0.5 mm), and the tube with the resin was immersed in nitrobenzene for several hours. An inner reference solution, which consisted of an aqueous solution of sodium chloride (0.1 M) and an appropriate sodium salt (0.1 M), was injected into the teflon tube, and the ion-selective electrode shown in Fig. 1 was constructed. The teflon tube was supported directly by a silver-silver chloride electrode. The performance of the electrode was examined by the emf measurement of the following electrochemical cell at room temperature (20 - 25 °C):
- SCE// Agar Salt Bridge (NH_4Cl or KCl)// Sample Solution/ Ion-selective Electrode +.
The selectivity of the electrode was evaluated by one of the mixed solution methods; namely, by the potential measurements in sample solutions containing fixed amount of a foreign ion and variable amounts of an ion for which the electrode was designed.[1)]

In Table I, the performance of the electrodes is summarized. In the concentration range of ion to be determined from 10^{-1} M to 10^{-4} M, the potential of the electrodes attained to stable and stationary value within a few minutes after the begining of the measurements. In lower concentration levels than 10^{-4} M, the response time longer than 5 minutes was observed. From pH of 3 to 10, the potential of these electrodes was independent of pH. Selectivity coefficients of the electrodes were almost the same orders of magnitude as those of corresponding liquid anion exchanger membrane electrodes.[2)]

Thus, the newly prepared resin was proved to behave effectively as the electrode membrane, when the resin of the appropriate anion form is impregnated with nitorbenzene. Such high selectivity observed in this work, probably, cannot be expected in usual anion exchange resins with hydrophilic sites, since the usual anion exchange resins are not suitable for the impregnation of a water-immiscible organic solvent, especially under the aqueous surroundings.

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Table I. Performance of Electrodes

Sensing Ion of Electrode(i)	Lower Limit of Nernstian Response (M)	Selectivity Coefficient (log K^{pot}_{ij})					
		(j): CH_3COO^-,	Cl^-,	Br^-,	I^-,	NO_3^-,	ClO_3^-
ClO_3^-	10^{-4}	-4.0	-2.6	-1.2	—	-0.4	—
NO_3^-	10^{-3} - 10^{-4}	-2.9	—	-1.1	+1.2	—	0.0
ClO_4^-	10^{-4} - 10^{-5}	—	-3.4	-2.8	-1.8	-2.6	—

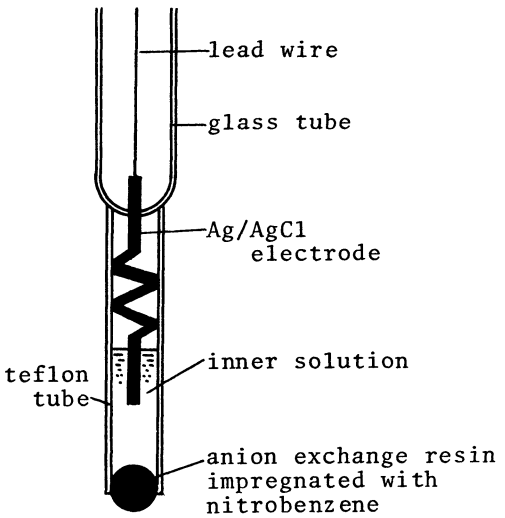

Fig. 1. Configuration of electrode

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2) J. Koryta, "Ion-selective Electrodes", Cambridge University Press, London, 1975, p. 120.

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