THE PREPARATION AND PROPERTIES OF LIQUID MEMBRANE ELECTRODES FOR p-AMINO BENZOIC ACID AND NICOTINIC ACID

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Abstract - The liquid membrane electrodes for measuring p-aminobenzoic acid and nicotinic acid were developed. Tetradecylammonium p-aminobenzoate ion pair complex and tetradecylammonium nicotinate ion pair complex were used as ion-exchangers of the electrodes. The electrodes were examined in terms of their effect of pore size of membrane, response curves, response time, pH of sample solution, temperature, selectivity coefficients and life-time. The slopes of calibration curves of p-aminobenzoate and nicotinate electrodes were -59.11 mV/decade and -59.12mV/decade in the linear parts, and coefficients of correlation were 0.9999 and 0.9997, respectively.

Key words - membrane electrode, p-aminobenzoic acid, nicotinic acid

p-Aminobenzoic acid and nicotinic acid are known as vitamin B complex. There has been much recent progress in the study of ion selective electrodes, but the electrodes for p-aminobenzoic acid and nicotinic acid were not reported. In this work, we prepared and tested the liquid membrane electrodes for determinations of p-aminobenzoic acid and nicotinic acid.

APPARATUS AND REAGENTS

Apparatus ----- The following apparatus were used. Digital multimeter (Advantest, Model. TR 68-45). Silver-silver chloride electrode (TOA Electronics Ltd., Model HS 205C), pH-meter (Hitachi-Horiba, Model F-7). Combination pH electrode (Orion Co., Model 94-04).

Reagents ----- Sodium p-Aminobenzoate, sodium nicotinate and other reagents used were of analytical-reagent grade from Wako Pure Chemical Industries, Ltd.

EXPERIMENTAL

Synthesis of ion pair complex

Tetradecylammonium p-amino-benzoate ion pair complex and tetradecylammonium nicotinate ion pair complex were prepared by mixing 1.5×10^{-3} mol solid silver p-aminobenzoate or solid silver nicotinate with 1.5×10^{-3} mol tetradecylammonium iodide in 30 ml of chloroform under stirring for 1 hour. The precipitates were filtered off and the filtrate was dried in vacuum. The elemental analysis for the complex agreed with the formation of 1:1 tetradecylammonium p-aminobenzoate ion pair complex; $[\text{NH}_2\text{C}_6\text{H}_4\text{COO}^- \cdot \text{N}(\text{C}_{10}\text{H}_{21})_4]$ or tetradecylammonium nicotinate ion pair complex; $[\text{C}_5\text{H}_4\text{NCOO}^- \cdot \text{N}(\text{C}_{10}\text{H}_{21})_4]$.

Preparation of the liquid membrane electrodes.

A membrane filter (tetrafluoroethylene resin) was fixed to one

Fig.1 The structure of liquid membrane electrode for p-aminobenzoic acid and nicotinic acid

end of glass tubing with silicone resin as shown in Fig. 1.

Tetradecylammonium p-aminobenzoate in nitrobenzene (10^{-2} M) or tetradecylammonium nicotinate in nitrobenzene (10^{-2} M) was used as ion-exchanger of the electrode. Sodium p-aminobenzoate or sodium nicotinate aqueous solution (10^{-2} M) saturated with silver chloride was used as the internal reference solution along with a silver-silver chloride internal reference electrode. The electrodes were conditioned in sodium p-aminobenzoate or sodium nicotinate solution (10^{-2} M) for 24 hours before use.

Determinations of sodium p-aminobenzoate and sodium nicotinate

Sodium p-aminobenzoate solution or sodium nicotinate solution was taken into the cell. Tetradecylammonium p-aminobenzoate or tetradecylammonium nicotinate liquid membrane indicator electrode and a silver-silver chloride reference electrode were soaked in this cell. Sample solution was stirred at 25°C and potential was measured. All sample solutions were aqueous solutions.

The liquid membrane electrodes were stored in 10^{-2} M sodium p-aminobenzoate solution or sodium nicotinate solution.

RESULTS AND DISCUSSION

The liquid membrane electrodes thus made were then examined in terms of their effect of pore size of membrane, response curves, response time, pH of sample solution, temperature, selectivity coefficients and life-time.

Effect of pore size of membrane

Pore size ($0.45\ \mu$, $0.22\ \mu$ and $0.10\ \mu$) of tetrafluoroethylene membrane filter (Sumitomo Electronics Ind., Fluoropore) for supporting membrane was discussed (Table 1 and 2). A linear relationship was obtained in the range of 10^{-4} - 10^{-1} M sodium p-aminobenzoate or sodium nicotinate solution with all membranes. The slopes were approximated by the Nernstian response (59.15 mV/decade).

Table 1 Effect of the pore size of tetrafluoroethylene membrane on the potential of p-aminobenzoate liquid membrane electrode.

Y = b X + a	p o r e s i z e (μ)		
	0.45	0.22	0.10
Linear range (M)	10^{-4} - 10^{-1}	10^{-4} - 10^{-1}	10^{-4} - 10^{-1}
Slope (mV / decade)	-58.35	-59.11	-58.80
Intercept (mV)	177.3	113.0	97.1
Correlation coefficient	0.9997	0.9999	0.9993

Table 2 Effect of the pore size of tetrafluoroethylene membrane on the potential of nicotinate liquid membrane electrode.

Y = b X + a	p o r e s i z e (μ)		
	0.45	0.22	0.10
Linear range (M)	10^{-4} - 10^{-1}	10^{-4} - 10^{-1}	10^{-4} - 10^{-1}
Slope (mV / decade)	-58.68	-59.03	-59.12
Intercept (mV)	82.55	73.25	62.90
Correlation coefficient	0.9996	0.9998	0.9997

Response time and response curve

The response times of the electrodes were less than 1 min in the concentration range of 10^{-5} – 10^{-1} M sodium p-aminobenzoate solutions and 10^{-5} – 10^{-1} M sodium nicotinate solutions. The slopes of calibration curves of p-aminobenzoate and nicotinate electrodes were -58.35 – -59.12 mV/decade in the linear part, and the coefficients of correlation were 0.9993 – 0.9999 . The calibration curve plotted against the concentration of nicotinate was shown in Fig. 2.

Effects of pH and temperature

The effect of pH of the sample solution on the response of the electrodes was examined in the range of pH 3.18 – 10.70. The constant response was observed at pH 4.01 – 9.96 in less than 3 mV. The effect of temperature on sodium p-aminobenzoate or sodium nicotinate determination was examined in the range of 15 – 50°C , too. The optimum temperature was 15 – 35°C . Therefore all subsequent measurements were done at pH 6.70 and 25°C .

Selectivity coefficients

Selectivity coefficients of the liquid membrane electrodes

Fig. 2 Calibration curve for sodium nicotinate using tetradecylammonium nicotinate liquid membrane electrode (pore size $0.10\ \mu$)

$$E = 62.90 - 59.12 \log C$$

E is the potential for sodium nicotinate at concentration, C.

Table 3 Selectivity of tetradecylammonium p-aminobenzoate liquid membrane electrode

Interfering substance	Selectivity coefficient*		
	Pore size (μ)		
	0.45	0.22	0.10
Sodium sulfate	1.39×10^{-2}	1.19×10^{-2}	1.64×10^{-2}
Dipotassium hydrogen phosphate	2.56×10^{-3}	2.62×10^{-3}	3.56×10^{-3}
Disodium hydrogen phosphate	2.74×10^{-3}	2.93×10^{-3}	4.22×10^{-3}
Nicotinamide	3.81×10^{-2}	2.75×10^{-2}	4.36×10^{-2}
Ascorbic acid	7.38×10^{-1}	7.42×10^{-1}	9.31×10^{-1}
Cyanocobalamin	3.14×10^{-3}	3.03×10^{-3}	5.41×10^{-3}
L-Cysteine	1.56×10^{-2}	1.67×10^{-2}	2.42×10^{-2}
Sodium glutamate	1.64×10^{-3}	1.32×10^{-3}	1.84×10^{-3}
L-Arginine	4.03×10^{-2}	4.17×10^{-2}	4.53×10^{-2}
β -Alanine	3.89×10^{-3}	3.47×10^{-3}	6.59×10^{-3}

* Separate-solution method. The selectivity was calculated from the e.m.f. of a solution containing p-aminobenzoate ion at activity 10^{-2} M, and a solution containing the interfering substance at activity 10^{-2} M.

Table 4 Selectivity of tetradecylammonium nicotinate liquid membrane electrode

Interfering substance	Selectivity coefficient*		
	Pore size (μ)		
	0.45	0.22	0.10
Sodium sulfate	1.45×10^{-2}	1.56×10^{-2}	1.04×10^{-2}
Dipotassium hydrogen phosphate	4.97×10^{-3}	5.35×10^{-3}	3.36×10^{-3}
Disodium hydrogen phosphate	4.99×10^{-3}	5.35×10^{-3}	3.56×10^{-3}
Nicotinamide	1.34×10^{-1}	1.49×10^{-1}	9.31×10^{-2}
Ascorbic acid	7.96×10^{-1}	6.98×10^{-1}	4.95×10^{-1}
Cyanocobalamin	6.80×10^{-3}	7.61×10^{-3}	6.70×10^{-3}
L-Cysteine	3.34×10^{-2}	3.92×10^{-2}	2.72×10^{-2}
Sodium glutamate	2.85×10^{-3}	3.15×10^{-3}	2.20×10^{-3}
L-Arginine	8.25×10^{-2}	7.20×10^{-2}	4.22×10^{-2}
β -Alanine	1.43×10^{-3}	1.68×10^{-2}	9.58×10^{-3}

* Separate-solution method. The selectivity was calculated from the e.m.f. of a solution containing nicotinate ion at activity 10^{-2} M, and a solution containing the interfering substance at activity 10^{-2} M.

were discussed for 10 compounds (sodium sulfate, dipotassium hydrogen phosphate, disodium hydrogen phosphate, nicotinamide, ascorbic acid, cyanocobalamin, L-cysteine, sodium glutamate, L-arginine, and β -alanine) by the separate-solution method. The results were shown in Table 3 and 4. The liquid membrane electrodes for measuring p-aminobenzoic acid and nicotinic acid were not seriously interfered by these concomitant compounds. Selectivity coefficients were calculated from the following relationship¹⁾;

$$\log k_{ij} = \frac{E_j - E_i}{2.303 RT / nF} + (1 - n/m) \log a_i$$

- k_{ij} : Selectivity coefficient
 (Primary ion i, interfering ion j)
 E_j : e.m.f. for the interfering ion j
 E_i : e.m.f. for the primary ion i
 R : Gas constant
 T : Absolute temperature
 F : Faraday's constant
 n : Charge of ion i
 m : Charge of ion j
 a_i : Activity of ion i

Life time of electrode

The electrodes were used 8 hours / day. Analytical values were almost constant for 5 - 30 days after preparation. They were stored in 10^{-2} M sodium p-aminobenzoate solution or sodium nicotinate solution, respectively.

REFERENCES

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