A Hydrogen Ion-Selective Poly(aniline) Solid Contact Electrode Based on Dibenzylpyrenemethylamine Ionophore for Highly Acidic Solutions

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Hydrogen-ion selective solid contact electrodes based on tribenzylamine, dibenzyl-naphthalenemethylamine, and dibenzylpyrenemethylamine ionophores were prepared. With these electrodes, we showed that the response ranges were influenced by the number of phenyl rings in the ionophores. The lower limits for a linear pH response in acidic solutions were pH 2.50, 0.65, and 0.50, respectively. As the number of phenyl rings in the ionophores increased, the slopes of the EMF responses of these electrodes did not change significantly, but their response extended toward an acidic range (shifted to pH 0.50). Thus, their dynamic response range became wider. A solid contact electrode with dibenzylpyrenemethylamine ionophore, in particular, showed the best selectivity, from the interference of cations and anions, and the best reproducibility of the EMF. This electrode was stored in Tris buffer solutions, artificial serum, and hydrofluoric acid solutions for one month without any loss of performance. Their response time was 8 s. Satisfactory results were obtained when it was tested directly with artificial serum (in pH range 6.0–8.5) and hydrofluoric acid.

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Introduction

Ion-selective electrodes (ISEs) are chemical sensors with the longest history, and still probably have the largest number of applications.¹ More recently, two types of potentiometric wire-type electrodes (WTEs), such as coated wire electrodes (CWEs)² and solid contact electrodes (SCEs),^{3,4} have exhibited rapid development. In WTEs, a total elimination of the internal filling solution provides new advantages. Simplicity of design, lower costs, mechanical flexibility, the possibility of miniaturization and microfabrication has widened the applications for WTEs in the fields of medicine and biotechnology. In SCEs of these two advanced types of WTEs, after polymerization, these polymer-coated metal electrodes were dipped into a PVC cocktail membrane solution until a bead was formed. Especially, these SCEs based on the electropolymerization method of amino derivatives onto the metal surface produced very good results, such as stabilization of the base potential, reproducibility, best selectivity, wide response ranges and fast response time.^{5,6} Thus, in recent years, there have been many reports on hydrogen ion-selective SCEs⁷ and hydrogen ion-selective ionophores.⁸ We have studied hydrogen ion-selective ionophores and SCEs in our laboratory.⁹ After Simon¹⁰ published information about tridodecylamine ionophore for hydrogen sensing, we synthesized various types of tertiary amine compound ionophores, and strived to understand the response characteristics of these ionophores.^{11–15} Particularly, after our result concerning SCE based on the

tribenzylamine (TBA) ionophore¹⁶ was published, which had a wider response range than the electrodes with tridodecylamine (TDDA) ionophore, many types of aromatic tertiary amine compound ionophores were synthesized and studied.^{17–21} We found that the response ranges shifted to an alkali range (toward pH 14) by extending the chain length between the phenyl ring and nitrogen in the ionophores, and were able to synthesize ionophores that exhibited a linear response up to pH 14.²² As can be seen in the various results published until now on aromatic and aliphatic ionophores, however, there have been no reports on ionophores that are particularly effective in a strong acidic solution.

In the present work, amine compound ionophores that could respond linearly to strong acid were synthesized, which has been noted as a limit of SPM (solvent polymeric membrane) ionophores,^{13–22} and response characteristic due to structural changes of the ionophores in strong acid were demonstrated. Especially, we examined the responses resulting from increasing numbers of phenyl rings in ionophores, which had not been previously studied. Additionally, other common pH response characteristics of all solid-state potentiometric sensors for hydrogen ion based on poly(aniline), covered with a plastic PVC membrane and activated by these ionophores, are presented and evaluated in terms of analytical applications, such as in artificial serum and HF solution.

Experimental

Reagents

Tetrahydrofuran (THF) was purified by vacuum distillation.

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Table 1 Response slope and response ranges of SCEs based on three ionophores in a Tris-buffered sample solution

	Response slope/mV pH ⁻¹	Response range/pH
TBA	55.1	2.50 – 11.20
DBNA	59.1	0.65 – 10.00
DBPA	56.4	0.50 – 10.20

For all of the experiments, analytical-grade chemical and doubly distilled demineralized water was used. High-molecular-weight polyvinylchloride (PVC, $n = 1, 100$), potassium tetrakis[4-chlorophenyl]borate (KTPCIPB), 2-nitrophenyloctyl ether (*o*-NPOE), aniline, pyrenemethylamine hydrochloride, naphthalenemethylamine, and tribenzylamine (TBA) were obtained from Aldrich Co.

Neutral carrier synthesis

In the laboratory, the *N*-alkylation of pyrenemethylamine hydrochloride and naphthalenemethylamine was performed to yield dibenzylpyrenemethylamine (DBPA). Also, dibenzyl-naphthalenemethylamine (DBNA) as ionophores, was synthesized based on a reaction with benzylbromide.²³ Two solutions of 0.01 mol pyrenemethylamine hydrochloride (naphthalenemethylamine) and 0.02 mol benzylbromide in 100 mL of benzene and NaHCO₃, KI and tetrabutylammoniumhydroxide (TBA-OH) in 100 mL of water were placed in a flask. The flask and the contents were heated in a 140°C oil bath, being stirred vigorously for 48 h. After cooling, a benzene layer was separated and extracted several times with H₂O. The solvent was removed *via* a rotatory evaporator, dried over MgSO₄ and chromatographed (with hexane:ethyl acetate = 40:1) to give a yellow oil. To identify and characterize the synthesized material, the followings were used: gas chromatography (Hewlett Packard 5890), NMR (Hitachi R-24B) and elemental analyzer (Fisons Co. EA 1108). Elemental analysis gave the following results. Calculated for dibenzylpyrenemethylamine: (411.55) 90.47% C, 6.13% H, 3.40% N; found, 89.88% C, 6.19% H, 3.93% N. For dibenzyl-naphthalenemethylamine: (337.46) 88.98% C, 6.87% H, 4.15% N; found 89.11% C, 6.84% H, 4.05% N.

Polymerization

Electrochemical experiments were performed in a conventional cell with three electrodes. A saturated calomel electrode was used as the reference electrode, and all potentials were recorded and reported with respect to this electrode. As the working and counter electrodes, platinum wire (1 mm in diameter) was used. Electropolymerization was carried out using cyclic voltammetry in 0.03 M aniline and 0.06 M HCl electrolyte on a platinum wire. Cyclic voltammograms were recorded using a Bi-potentiostat (Pine instrument company Model AFRDE5) and X-Y recorder (YOKOGAWA Model 3025). For the electrochemical polymerization of aniline, the potential was swept between 0.0 V and 1.0 V *vs.* SCE at a scan rate of 100 mV/s. The potential cycling was repeated up to 50 cycles and stopped at 1.0 V. After electrodeposition, the poly(aniline) was washed with distilled water, and then the poly(aniline) was dried for 24 h in an 80°C oven.

Preparation of a cocktail solution and a solid contact electrode

A cocktail solution contained 3.00 wt% ionophore (TBA, DBPA, and DBNA, respectively), 0.800 wt% KTPCIPB, 64.2 wt% *o*-NPOE and 32.0 wt% PVC.²⁴ All components were

Fig. 1 Response characteristics of SCEs based on TBA, ■; DBNA, ▲; DBPA, ●.

dissolved in THF. The surface of the poly(aniline) film was covered with this cocktail solution.

EMF measurements

The EMF values were measured at $20 \pm 0.2^\circ\text{C}$ using a Model 355 ion-analyzer (Mettler-Toledo Ltd. England). In all experiments, the measurements of the sample solutions were determined with a Mettler-Toledo Inrab 412 glass electrode. The external reference electrode was a double-junction calomel electrode, Orion 90-20-00 (Orion Research, USA). The pH of the Tris-NaOH buffer solution was adjusted by the addition of hydrochloric acid in the pH range of 0.2 – 14.0. The standard deviation arising from this equipment was < 0.1 mV for a single determination. Before use, the electrodes were conditioned in distilled water for at least 2 h. The selectivity factors were determined by a fixed interference method using solutions of 0.01 M Tris(hydroxymethyl)aminomethane, 0.03 M sodium hydroxide and 0.13 M sodium chloride.²⁵ To analyze the influence of other interfering ions, KCl, LiCl, NaNO₃, NaBr, NaI, NaSCN were used to replace NaCl.

Results and Discussion

The pH response characteristics of SCEs based on TBA, DBNA, and DBPA ionophores in Tris buffer solutions are presented in Table 1 and Fig. 1. In Table 1, we compare the slopes of the EMF responses and the response range of the SCEs based on the TBA ionophore with those based on the DBNA and DBPA ionophores, the slopes of the EMF responses showed 55.1, 59.1, 56.4 mV pH⁻¹ (at $20 \pm 0.2^\circ\text{C}$), respectively. The linear dynamic ranges for the pH response were pH 2.50 – 11.20 for TBA-based SCEs, pH 0.65 – 10.00 for DBNA and pH 0.50 – 10.20 for DBPA. When the slopes of the EMF responses, the response range, and dynamic ranges were considered, the slopes of the EMF responses of these electrodes showed minimal differences among the three differences as the numbers of phenyl ring in the ionophore increased. However, the dynamic ranges and linear-response ranges of these SCEs were closely related to the number of phenyl rings in the ionophores. Namely, as the number of phenyl rings in the ionophore increased, their dynamic ranges became wider and their response ranges shifted toward an acid range (shifted to pH 0.5). These results and the structures of TBA, DBNA, and DBPA ionophore are given in Fig. 2. This appeared to be caused by an increase in the electron donation ability of nitrogen atom in amine compound ionophores.

The selectivity coefficients with respect to Na⁺, K⁺, and Li⁺ were evaluated by a fixed-interference method. The resulting

Table 2 Response limit of SCEs in a Tris-buffered sample solution with 0.13 M cation and anion background

0.13 M of interference ion	$-\log K_{\text{HM}}^{\text{pot}}$			$-\log K_{\text{HX}}^{\text{pot}}$				
	M = Na ⁺	M = K ⁺	M = Li ⁺	X = Cl ⁻	X = Br ⁻	X = NO ₃ ⁻	X = SCN ⁻	X = I ⁻
TBA	10.01	8.72	10.62	2.54	2.60	2.69	3.97	3.85
DBNA	10.00	9.91	10.00	1.69	1.33	1.37	2.31	1.49
DBPA	10.20	9.60	10.20	0.50	0.50	0.50	1.70	1.00

Table 3 Common response characteristics of SCEs based on three ionophores in a Tris-buffered sample solution

Ionophore	Stabilization time/min	Response time/s	Standard deviation/mV	
TBA	About 120	8	1.0 (in pH 6.50)	0.5 (in pH 8.50)
DBNA	About 60	11	1.3 (in pH 6.50)	3.8 (in pH 8.50)
DBPA	About 48	8	1.0 (in pH 6.50)	1.9 (in pH 8.50)

values of $-\log K_{\text{HM}}^{\text{pot}}$ for the SCEs, based on TBA, DBNA, and DBPA ionophores, are presented in Table 2. The selectivity of these electrode showed that the common ions of alkali metals would not cause any significant interference, as long as the concentrations of the metals in a sample solution were not too high. However, this membrane showed somewhat less selectivity over K⁺. This seems to be related to the low solubility of the complex of the interfering ions with TpCIPB⁻¹⁶. The effects of anions on the pH response are also shown in Table 2. The following sequence of anion interference was observed: SCN⁻ > I⁻ > NO₃⁻, Br⁻, and Cl⁻. The effect of the nature of the anion on the DBPA ionophore-based SCEs were strongest in SCN⁻, milder in I⁻ and least with Cl⁻, Br⁻, and NO₃⁻. However, when we compared other tertiary amine ionophores based SCEs, the effect of the nature of the anion on the TBA, DBNA, and DBPA ionophores based SCEs was least in these five interfering anion species commonly existing in water.

The stability of the EMF measurements for SCEs based on these ionophores was measured in a pH 7.47 Tris buffer; the results are given in Table 3. Especially, for SCEs based on DBPA, within the first 30 min while measuring the EMF value, they changed rapidly and irregularly. However, after 15 min they became stabilized, and the change in the EMF was less than 1 mV. The potential drift of these electrodes became stabilized within 2 h. Thus, before using these electrodes, we had to condition all of the electrodes in distilled water or in a pH 7.47 Tris buffer for at least over 2 h. The response time of the electrodes based on these ionophores that was obtained by injecting hydrochloric acid into a Tris buffer solution, is given in Table 3. Their response time was less than 11 s. These electrodes were continuously kept in a Tris 7.47 buffer and artificial serum for one month, while maintaining a stabilized response potential without any loss of performance. These electrodes, which were dried after daily measurements in Tris buffer sample solutions, maintained a stable electrode potential for more than 1 year, suggesting that they can be used for over 1 year. The reproducibility of EMF measurements using these electrodes was checked by alternating measurements (10 min each) in two Tris buffer solutions of pH 6.5 and 8.5, respectively (20 ± 0.2°C). The standard deviation for the determined EMF differences was less than 1.3 mV (N = 10) in a Tris buffer solution of pH 6.5, and less than 3.8 mV in a Tris buffer solution of pH 8.5 (Table 3).

As expected from the selectivity data given above, there was

Fig. 2 Structures of TBA, DBNA, and DBPA ionophores and their response ranges of SCEs based on these ionophores.

Fig. 3 pH responses for SCEs containing DBPA ionophore to Tris-buffered sample solution, $\blacktriangle$; to Tris-buffered sample solution with 24 mM NaHCO₃, $\blacktriangledown$; and to artificial serum, $\blacksquare$.

no interference from electrolytes in artificial serum in the physiologically relevant pH range (pH 6.0 – 8.5), Fig. 3. In artificial serum, the slopes of the EMF responses of the electrodes showed 54.9 mV (55.1 mV in Tris buffer sample solution) for TBA-based SCEs, 55.0 mV (59.1 mV) for DBNA and 54.6 mV (56.4 mV) for DBPA. The addition of a typical extracellular concentration of hydrogen carbonate ions (24 mM) to the Tris-buffered solutions did not significantly influence the slope of the electrode response. In a Tris-buffered sample solution containing 24 mM hydrogen carbonate ions, the response slopes of these electrodes showed 55.0 mV/pH, 58.8 mV/pH and 56.4 mV/pH, respectively (20 ± 0.5°C). The measured results in artificial serum had almost the same values as those measured in Tris-buffered pH solutions and in a Tris-buffered pH solution with 24 mM hydrogen carbonate ions. Thus, it was not affected by the electrolyte ions existing in the artificial serum. This result underlines the fact that SCEs containing these ionophores eliminate the observed EMF effect of CO₂ diffusion across the membrane.

There was no erosion effect for the SCEs based on TBA,

Fig. 4 E-V curve for the titration of SCEs based on DBPA ionophore in HF solution with an NaOH solution.

DBNA, and DBPA ionophores as a pH sensor in hydrofluoric acid. These electrodes can be used for end-point indication in the titration of hydrofluoric acid with sodium hydroxide. Figure 4 shows an E-V curve for this type of titration using a sample of 50 ml of 0.04 M HF titrated with 0.05 M NaOH for SCEs based on the DBPA ionophore. The HF concentration was found to be 0.0405 M with a standard deviation of 0.002 M ($n = 5$). We found that this electrode showed the best reproducibility without any erosion when it was stored in a hydrofluoric acid solution. After a measurement of this electrode in a hydrofluoric acidic solution, the potential response characteristics in the Tris-buffered pH sample solution were not changed. Their linear dynamic range remained at pH 0.50 – 10.20, and the Nernstian slope showed 56.4 mV/pH (at $20 \pm 0.2^\circ\text{C}$) after being used in a hydrofluoric acidic solution.

Conclusions

The pH response characteristics of SCEs based on TBA, DBNA, and DBPA ionophores were compared in a Tris-buffered pH sample solution. Their linear limits in the pH response in acidic solution were pH 2.50, 0.65, and 0.50, respectively. As the number of phenyl rings in the ionophores increased, the slopes of the EMF responses of these electrodes do not exhibit much difference, their linear response ranges, however, were moved toward a more acidic range (shifted to pH 0.50), and their dynamic range became wider. The response time of SCEs based on DBPA ionophores, obtained by the injection of hydrochloric acid into a Tris buffer sample solution, was 8 s, and their stabilization time was about 48 min. The standard deviation in the determined EMF differences was less than 1.3 mV for Tris buffer solutions of pH 6.5, and less than 3.8 mV for Tris buffer solutions of pH 8.5. When it was directly applied to human whole blood (in pH range 6.0 – 8.5), we could obtain the same results, which were satisfactory. This electrode could be stored in a pH 7.47 Tris buffer solution, artificial serum and a hydrofluoric acidic solution for one month without any loss of performance. Hydrofluoric acid did not erode the surface of this electrode, and its stability was

maintained without showing any changes in potentials after being used in a hydrofluoric acid solution.

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