Polymeric Acetate-Selective Electrodes Based on *meso*-($\alpha,\alpha,\alpha,\alpha$)-Tetrakis-[(2-arylphenylurea)phenyl]porphyrins: Electronic and pH Effects

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Received July 3, 2002

Polymeric membrane electrodes for acetate anion based on *meso*-($\alpha,\alpha,\alpha,\alpha$)-5,10,15,20-tetrakis[2-(pentafluorophenylurea)phenyl]porphyrin **I** and similar urea-functionalized porphyrins **II-IV** as neutral ionophores were prepared. The membrane based on porphyrin **I** exhibits the best potentiometric properties in pH 6.0 rather than pH 7.0: linear stable response over a wide concentration range (6.0×10^{-5}-1.0×10^{-2}) with a slope of -59.6 mV/decade and a detection limit of $\log[CH_3COO^-]$ = -5.32. Selectivity coefficients obtained from the matched potential method (MPM) in pH 6.0 indicate that interferences of hydrophobic anions are very small for the membranes of porphyrins **I** and **II** having the strong withdrawing group. The electronic effect of urea-functionalized porphyrins and pH effect of buffer solutions are discussed on the potentiometric response.

Key Words : Polymeric membrane, Urea-functionalized porphyrin, Acetate ion, Ion-selective electrode, Neutral ionophore

Introduction

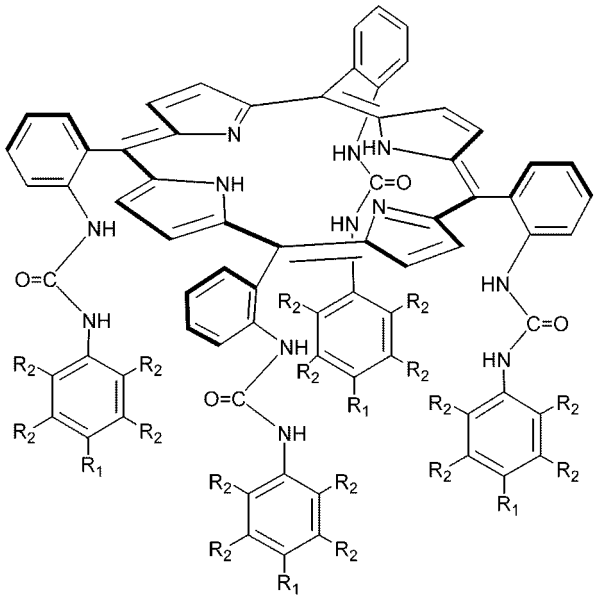
Many cations can be selectively and sensitively determined by direct measurement with ion-selective electrodes (ISEs), but the selective determination of many anions has a crucial drawback such as the classical Hofmeister series which is correlated with a preference for hydrophobic anions. Therefore, the need for ionophores with improved selectivities and sensitivities in the field of anion-selective electrodes is increased. The determination of acetate anion is very important in food science, especially fermentation processes. Enzymatic methods for the determination of acetate ion were developed, but they use biological enzymes as well as time-consuming.[1,2] Analytical methods for the determination of acetate anion include spectrophotometry,[3,4] electrochemistry,[5,6] and chromatography.[7,8] Among them, it was known that potentiometric analysis by ISE is simple, rapid, and less expensive. The first potentiometric response for the analysis of acetate was studied using a gas-permeable membrane that was used in Severinghaus-type sensors[5,6] and flow injection analysis systems to separate acetic acid vapor from the sample solution. These methods suffer from high detection limits and interferences such as H_2S, HNO_2, SO_2, CO_2 in acidic solutions. Many ISEs and bulk optodes have so far been developed by using ionophores for carboxylates, but are selective for carbonate or lipophilic carboxylates rather than for acetate.[9-11] Although metalloporphyrins were used as ionophores of anions in polymeric membranes,[12-14] but porphyrin derivatives were usually employed as ionophores of cations.[15-18] However, potentiometric sensor for acetate has been recently developed based on a *meso*-($\alpha,\alpha,\alpha,\alpha$)-tetrakis[2-(4-fluorophenylurea)phenyl]porphyrin without metal centers that form hydrogen bonds to the acetate ion.[19] The ISEs respond more strongly to acetate in pH 7.0 buffer solutions than to Cl^- which forms highly stable 1 : 1 complexes in DMSO-d_6.

In the present study, we will describe the preparation and characterization of acetate-ISEs based on urea-functionalized porphyrins as neutral ionophores. The electronic effect of urea-functionalized porphyrins and pH effect of buffer solutions are described on the potentiometric response. The ISE based on *meso*-($\alpha,\alpha,\alpha,\alpha$)-tetrakis[2-(pentafluorophenylurea)phenyl]porphyrin (**I**) having the strong withdrawing group exhibits improved sensitivity, selectivity, and lifetime for acetate anion in pH 6.0 buffer solutions.

Experimental Section

Reagents. Urea-functionalized porphyrins (**I-IV**) tested as acetate ionophores were prepared according to the procedure described previously,[19] and they are shown in Figure 1. High molecular weight PVC, dioctyl sebacate (DOS), dioctyl adipate (DOA), dioctyl phthalate (DOP), 2-nitrophenyl octyl ether (*o*-NPOE), tridodecylmethylammonium chloride (TDDMACl) and tetrahydrofuran (THF), which were obtained from Fluka, were used to prepare the PVC membranes. Analytical grade sodium and potassium salts of tested anions were used. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions.

Preparation of polymeric ion-selective electrodes. The compositions of PVC-based acetate-selective electrodes were summarized in Table 1, and the typical one was 33 mg PVC, 66 mg plasticizer, 1 mg ionophore and TDDMACl (50 mol% of ionophore). The ionophore, plasticizer and PVC were dissolved in the appropriate volume of THF and mechanically stirred. All membrane cocktails were cast in glass rings placed on glass plates for conventional ion-selective electrodes. Solvent from PVC membrane was allowed to evaporate for at least 24 hours at room



I. R_1, R_2 = F
II. R_1 = F, R_2 = H
III. R_1, R_2 = H
IV. R_1 = CH_3, R_2 = H

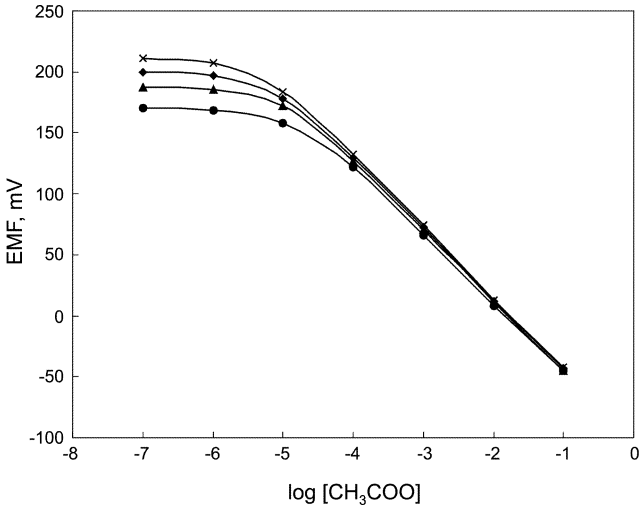
Figure 1. Structures of urea-functionalized porphyrins **I-IV** used in the acetate-ISEs.

temperature. The thickness of the resulting membrane was about 0.3 mm.

Potentiometric measurements. The electrochemical properties of acetate-selective electrodes were investigated in the conventional configuration. Small disks were punched from the cast membranes and mounted in Philips electrode bodies (IS-561). For all electrodes, 0.1 M KCl was used as an internal filling solution. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference electrode (Model 90-02). The electrochemical potential was measured using 16-channel potentiometer coupled to a computer. The dynamic response curves were produced by adding standard solutions of anions to magnetically stirred buffer solution (0.05 M HEPES-LiOH). The selectivity coefficients ($\log K^{pot}_{acetate,j}$) were determined by the matched potential method (MPM). At least three times measurement were performed, and the data were determined from the plot.

Results and Discussion

Host compounds as an anion ionophore should satisfy certain conditions. They should bind selectively specific anion, and have kinetically fast exchange and sufficiently lipophilicity. The pH dependence of potentiometric response was investigated in different pH (5 to 8) buffer solutions. The effect of pH on the potentiometric response of the novel electrode prepared with urea-functionalized porphyrin **I** as an ionophore (66 mg o-NPOE, 33 mg PVC, 50 mol% TDDMACl, and 1 mg urea-functionalized porphyrin **I**) is studied in 0.05 M HEPES-LiOH buffer solutions at different pH values, and shown in Figure 2. The results indicate that the potentiometric response to acetate depends on the buffering pH values. According to experimental results, when the solution pH was increased from 5 to 8, the slope and detection limit of the membrane was slightly changed. The better slope and detection limit was obtained at pH 6: the



Ionophore	pH	Slope (mV/decade)	Detection Limit (log[CH_3COO^-])
	5 (◆)	-58.9	-51.8
	6 (×)	-59.6	-5.32
	7 (▲)	-58.2	-5.03
	8 (●)	-57.1	-4.88

Figure 2. The potentiometric responses of the novel electrodes prepared ionophore **I** in 0.05 M HEPES-LiOH buffer solutions at different pH values.

Table 1. Selectivity coefficients of PVC-based acetate selective membranes in pH 6 HEPES-LiOH buffer solutions.

Ionophore	Slope (mV/decade)	Detection Limit (log[CH_3COO^-])	log $K^{pot}_{CH_3COO^-,j}$							
			j = HSO_3^-	j = HCO_3^-	j = I^-	j = Br^-	j = ClO_4^-	j = NO_2^-	j = SCN^-	j = NO_3^-
I	-59.6	-5.32	-2.19	-2.13	-1.96	-1.89	-1.71	-1.69	-0.88	-0.02
II	-57.5	-5.20	-2.15	-2.33	-2.27	-2.12	-1.97	-1.99	-1.13	-0.08
III	-53.6	-5.03	-2.46	-3.16	-2.72	-1.81	-3.63	-1.93	-0.45	+0.47
IV	-50.8	-4.95	-1.42	-1.86	-0.96	-0.91	-0.37	-0.50	+0.45	+0.49
II[a]	-54.8	-4.51	-0.56	-1.34	+0.20	-0.13	+0.12	+0.21	+0.60	+0.68

[a]In pH 7 HEPES-NaOH buffer solution (ref. 19)

slope of -59.6 mV/decade and the detection limit of $\log[CH_3COO^-]$ = -5.32. This Nernstian is for a monovalent anion response. When considering the different values of initial potential at different pHs in Figure 2, the hydroxide anion activity affects the potentiometric response of the membrane. It can be concluded that the membrane exhibits excellent response to acetate about pH 6.0. The effect of the buffer strength was also evaluated. When the molarity of the HEPES-LiOH (pH 6.0) was more than 0.05 M, the buffering capacity for some strongly acidic and basic anions was satisfied within the anion concentrations tested. All remaining experiments were performed using a 0.05 M HEPES-LiOH.

The anion-ISE membranes were prepared with urea-functionalized porphyrins (**I-IV**) as an ionophore and studied for potentiometric response to several anions. They have different electronic effect in urea-phenyl moiety of porphyrins. As it was mentioned, the potentiometric responses of PVC polymeric membranes containing urea-functionalized porphyrins (**I-IV**) for acetate anion-selective electrode were extensively studied in pH 6.0 solutions. The typical composition was 50 mol% TDDMACl *vs*. ionophore, 33 mg PVC, 66 mg plasticizer, and 1 mg ionophore **I-IV**. Figure 3 illustrated the electronic effect of urea-functionalized porphyrins on potentiometric response, and the potentiometric results for acetate were shown in Table 1. The ISE based on urea-functionalized porphyrin **I** exhibits a linear stable response over a wide concentration range (6.0×10^{-5}-1.0×10^{-2}) with a slope of -59.6 mV/decade and a detection limit of $\log[CH_3COO^-]$ = -5.32. Among the membranes prepared from urea-functionalized porphyrins (**I-IV**), the urea-functionalized porphyrin **I** gives the good sensitivity and Nernstian slope. These results imply that the urea-functionalized porphyrin **I** having the strongly withdrawing group may effectively bind with acetate anion in the polymeric membrane. The responses of the membrane to eight interfering anions were tested under the determined optimal conditions. Using an electrode based on a quaternary ammonium salt (TDDMACl), the potentiometric response follows the Hofmeister series, ClO_4^- > SCN^- > Salicylate > I^- > NO_3^- > NO_2^- > Br^- > Cl^-, HSO_3^- > CH_3COO^-, HCO_3^- > HSO_4^-. The selectivity pattern can also be seen in Table 1, and reflects the average response of the electrode to three to more tests with each anion in pH 6 buffer solutions. The selectivity series of the membrane containing ionophore **I** or **II** gives the follow as CH_3COO^-, NO_3^- > SCN^- > ClO_4^-, NO_2^- > Br^- > I^- > HSO_3^-, HCO_3^-. These ionophore-based ISEs exhibited excellent selectivity for acetate over every anion tested. The previous result is also shown in Table 1 which was obtained in pH 7 HEPES-NaOH buffer solutions.[19] Based on the membrane containing ionophore II, selectivity coefficients for acetate over several anions are improved in pH 6 compared with those obtained in pH 7. The result indicates that porphyrins **I** and **II** having the strongly withdrawing group may selectively bind with acetate anion in the polymeric membrane under the condition of pH 6.

The effect of plasticizers used was investigated in PVC polymeric membranes containing 1 mg ionophore I, 50 mol% TDDMACl vs. ionophore, 33 mg PVC, and 66 mg plasticizer. Figure 4 illustrates the acetate calibration curves for their electrodes in 0.05 M HEPES-LiOH pH 6.0 buffer solutions. Because membranes prepared from *o*-NPOE showed the best detection limit, the best linear range, and Nernstian slope for acetate, *o*-NPOE was chosen as a proper plasticizer for use in the acetate-ISE membranes.

The response time of the ionophore-based membrane electrode ranged from less than 10 sec at all concentrations of acetate, and these novel prepared electrodes do not display any hysteresis effects.

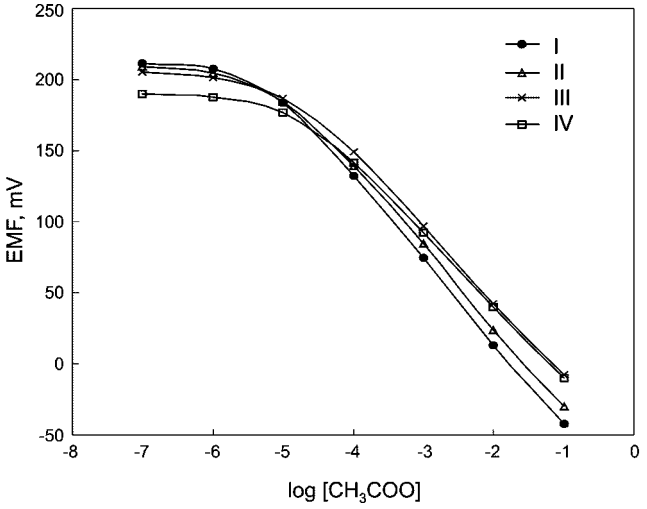
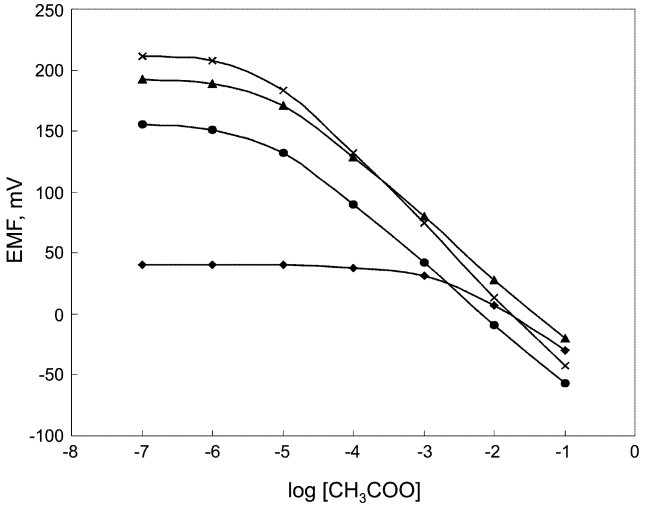
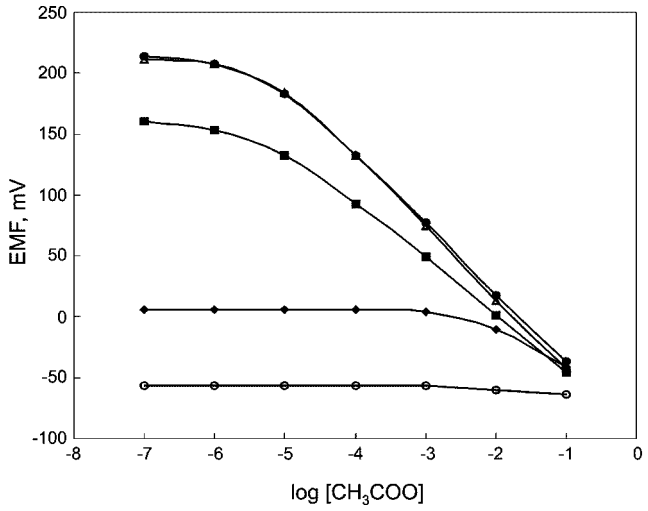


Figure 3. The potentiometric responses of the electrodes prepared ionophore **I-IV** in pH 6 buffer solutions.



Ionophore	Plasticizer	Slope (mV/decade)	Detection Limit ($\log[CH_3COO^-]$)
I	*o*-NPOE (×)	-59.6	-5.32
	DOS (◆)	-15.5	-4.00
	DOA (▲)	-50.3	-5.26
	DOP (●)	-49.6	-5.31

Figure 4. The acetate calibration curves for membranes prepared from different plasticizer with ionophore **I** in pH 6 buffer solutions.



Ionophore	Additive (%)[a]	Slope (mV/decade)	Detection Limit (log[CH_3COO^-])
I	0 (○)	-1.70	-3.72
	10 (◆)	-8.40	-3.80
	30 (■)	-45.6	-5.26
	50 (△)	-59.6	-5.32
	100 (●)	-57.4	-5.30

[a]mol% of Ionophore. Additive: TDDMACl.

Figure 5. The acetate calibration curves as a function of additive percentages for the membrane containing ionophore **I** in pH 6 buffer solutions.

The percentage of ion-exchanger (TDDMACl) used in the membranes is optimized by preparing membranes with 66 mg *o*-NPOE, 33 mg PVC, 1 mg ionophore I, and differing percentages of the additive, ranging from 0 to 100 mol% of the ionophore. Figure 5 shows the acetate calibration curves as a function of additive percentages in 0.05 M HEPES-LiOH pH 6.0 buffer solutions. The different slopes were obtained by calibrating the ISE in different additive percentages. The worsening of the detection limit and slope below and above 50 mol% may be explained by the strong influence of ion-exchanger as an additive compound. The optimal formulation is when 50 mol% additive is used.

The stability of these membranes was measured as a function of time. The membranes are stored in 0.05 M HEPES-LiOH pH 6.0 buffer solutions when not in use. It was well known that the membrane components in PVC-based ISEs bleed into solution over time, resulting in a degradation of the performance of the membranes. The decrease of the sensitivity in the polymeric membrane may be dependent upon the lipophilicity of an ionophore, which can result in the ionophore bleeding from the membrane. Since urea-functionalized porphyrins (**I-IV**) as ionophores are neutral compounds having high lipophilicity, the membranes based on them should produce slow bleeding of ionophore. The stability of these membranes was evidenced in both the slopes of the calibration curve and the detection limits. After 15 days, the electrodes were responding at 97% of the initial response. By the end of one month, the response observed were still responding at 90% of the initial value. The long lifetime of the membrane as the acetate-ISE is due to the relatively high lipophilicity of the neutral ionophores tested in the membrane.

Conclusions

The potentiometric propeties are dependent upon the electronic effect of urea-functionalized porphyrin derivatives and buffering pH. Among the various membranes, the acetate-ISE prepared from porphyrin **I** having the strong withdrawing group may effectively and selectively bind with acetate anion in the polymeric membrane under the condition of pH 6. The membrane based on urea-functionalized porphyrin **I** exhibits a linear stable response over a wide concentration range (6.0×10^{-5}-1.0×10^{-2}) with a slope of -59.6 mV/decade and a detection limit of log[CH_3COO^-] = -5.32, and the selectivity series of the membrane gives the follow as CH_3COO^-, NO_3^- > SCN^- > ClO_4^-, NO_2^- > Br^- > I^- > HSO_3^-, HCO_3^-. The membrane was found to be chemically and physically stable, and made steady potential in 10 seconds with high reproducibility. The long lifetime of the membrane as the acetate-ISE is due to the relatively high lipophilicity of urea-functionalized porphyrins as neutral ionophores in the membrane.

Acknowledgment. This work was supported by the grant No. (R05-2001-000-00242-0) from the Basic Research Program of the Korea Science and Engineering Foundation.

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