Additive-Salt Effect on Low Detection Limit and Slope Sensitivity in Response of Potassium- and Sodium-Selective Neutral Carrier Based Electrodes and Their Liquid-Membrane Based Ion-Sensitive Field-Effect Transistor

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The remarkable effect of additive salts on low detection limits as well as slope sensitivities were observed for the response characteristics of bis(crown) and valinomycin based poly(vinyl chloride) (PVC) membrane electrodes. The low detection limits and the slope sensitivities for bis(crown) and valinomycin based PVC membrane electrodes were improved apparently as the hydrophobicity of the additive salts increases. In order to clarify the effect of additive salts of the PVC membrane electrodes, the response characteristics of liquid-membrane based K⁺ and Na⁺-ISEs, which were fabricated by using micro-ion-sensitive field-effect transistors (μ -ISFETs), were evaluated. The low detection limits and the slope sensitivities in the responses of the neutral-carrier based K⁺ and Na⁺- μ -ISFETs also changed remarkably with the kind as well as the concentration of the additive salts.

Keywords Additive salts, response behavior, ion-selective electrode, neutral carrier, liquid membrane, potassium and sodium ion-sensitive field-effect transistor

A neutral-carrier based ion-selective electrode (ISE) membrane consists of a neutral carrier, a membrane solvent, a membrane matrix (poly(vinyl chloride), PVC) and an additive salt. Sodium tetraphenylborate (NaTPB) and its more lipophilic derivative, tetrakis(*p*-chlorophenyl) borate (K-TCPB), are usually used as the additive salt. These additive salts have been reported to improve electrochemical characteristics of the neutral-carrier based ISEs taking account of the following advantages: reduction or elimination of interference by lipophilic anions^{1,2}, reduction of electrical resistance of the sensing membrane³, reduction of the electrode response time⁴ and enhancement of selectivity.^{5,6}

Recently, Bakker *et al.*^{5,6} have investigated the effect of additive salts on selectivity of the neutral-carrier based ISEs using an electrochemical method. Simon *et al.*^{7,8} reported that the selectivity of neutral-carrier based liquid membrane electrode is largely dependent on the amount of additive salts and can be improved to a large extent by the optimization of the ionic sites/car-

rier ratio. However, few reports concerning the effect of additive salts on the low detection limit and the slope sensitivity in the response characteristics of the neutral-carrier based ISEs have been published. Wakida *et al.* found that the low detection limit and the slope sensitivity in the response of a bis(12-crown-4) based Na⁺-ISE were remarkably enhanced using a hydrophobic tetraphenylborate derivative as an additive salt.⁹ It is valuable to examine other neutral carrier based ISEs as well as bis(12-crown-4) based ones to generalize the effect of additive salts on the low detection limit and the slope sensitivity. The object of this paper is to investigate the effect of additive salts systematically. It has been reported that anionic sites or ionic impurities are present in PVC.¹⁰⁻¹⁵ The effect of additive salts on the low detection limit and the slope sensitivity for the neutral-carrier based PVC membrane ISEs may be influenced by anionic sites.¹⁰⁻¹⁵

The effect of anionic sites present in PVC on additive salts in the response of the neutral-carrier based ISE will be eliminated using PVC-free liquid-membrane based micro-ion-sensitive field-effect transistors(μ -

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ISFET).^{16,17}

In the previous paper, we briefly reported the response of a K^+ -selective liquid membrane based μ -ISFET, whose sensing membrane contains valinomycin and several kind of additive salts, in order to evaluate the effect of the additive salts on the response of the electrodes.¹⁸ In this paper, we report response characteristics of K^+ and Na^+ -selective liquid membrane based μ -ISFETs and a PVC membrane based K^+ - and Na^+ -ISEs with the additive salts in their membranes.

Experimental

Chemicals

Bis(12-crown-4) (B12C4) and bis(benzo-15-crown-5) (B15C5) used as neutral carriers were obtained from Dojindo Laboratories (Kumamoto, Japan). Valinomycin (val) was obtained from Fluka Co. (Buchs, Switzerland). 2-Nitrophenyloctyl ether (NPOE) as a liquid membrane solvent was obtained from Dojindo Laboratories. Sodium salts of TPB derivatives, tetraphenylborate (TPB), tetrakis(4-fluorophenyl)borate (Cesibor), tetrakis(4-chlorophenyl)borate (TCPB) and tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (TFPB) were used for Na^+ - μ -ISFETs. The sodium salts of TPB, Cesibor and TCPB were obtained from Dojindo Laboratories. TFPB were obtained from Fluka Co. Potassium salts of TPB derivatives were prepared from their sodium salts by precipitating by mixing 50 ml of 10^{-2} M solution of the corresponding Na salt with the same volume of 10^{-2} M KCl solution. The resulting white precipitate was filtered, thoroughly washed with distilled water, and dried at room temperature. These salts were used as additive salts for a K^+ -ISE and a K^+ - μ -ISFET. PVC was obtained from Wako Pure Chemicals Co., Osaka, Japan. All other chemicals were of guaranteed grade.

Evaluation of the response of PVC membrane-based ISEs and liquid membrane based μ -ISFETs

The liquid membranes for a Na^+ - μ -ISFET and a K^+ - μ -ISFET were prepared using B12C4 and val or B15C5 as a neutral carrier, and sodium and potassium salts of TPB derivatives as an additive salt, respectively. A liquid membrane solvent for both μ -ISFET was NPOE. The concentration of the additive salts in the liquid membrane was adjusted to 33 or 67 mol% relative to the neutral carrier. In order to examine the concentration dependence of the additive salt in the liquid membrane for a K^+ - μ -ISFET, the concentration of the potassium salts of Cesibor was changed from 19 to 133 mol% relative to the neutral carrier. The preparation of the μ -ISFET was performed in the same manner as that described in the previous paper.¹⁶ The responses of the Na^+ - and K^+ - μ -ISFET to Na^+ and K^+ ions were examined by measuring the *emf* of the following electrochemical cell with an ISFET/mV meter (Shindengen Co., Saitama, Japan) at room temperature.

(-) $Ag/AgCl/3\text{ M }KCl/1\text{ M }CH_3COOLi/NaCl$ or KCl sample solution/ Na^+ or K^+ -selective liquid membrane with additive salts/FET (+)

The neutral carrier based PVC membrane for K^+ -ISE was prepared by casting a tetrahydrofuran (THF) solution containing 0.04 g of neutral carrier (val or B15C5), 0.8 g of NPOE, 0.4 g of PVC and 0.02 g of potassium salt of TPB derivatives onto a flat-bottomed glass dish of inside diameter 6.8 cm and by evaporating the solvent THF under 2 d standing at room temperature. Disks of about 0.4 cm diameter were cut out from the membrane. One of the disk membranes was fitted to an ion-selective electrode body. The response of the PVC membrane based K^+ -ISE to K^+ ion was examined by measuring the *emf* of the following electrochemical cell with an ion meter (Model 902A, Orion Research Inc., Boston, MA, USA) at room temperature.

(-) $Ag/AgCl/3\text{ M }KCl/1\text{ M }CH_3COOLi/KCl$ sample solution/PVC membrane/inner solution (10^{-2} M KCl)/ $AgCl/Ag$ (+)

The primary ion (Na^+ and K^+) solution was prepared without adjusting pH and ion strength. Activity coefficients were calculated according to Debye-Hückel equation. The detection limit was defined as primary ion activity at which the potential deviated by 18 mV from the extrapolation of the linear portions of the calibration curve.

Results and Discussion

Response of PVC membrane based K^+ -ISEs based on various kinds of TPB derivatives

The response of valinomycin and B15C5 based K^+ -ISEs with various kinds of TPB derivatives are shown in Figs.1(a) and 1(b), respectively. A remarkable effect of additive salts on the low detection limit as well as the slope sensitivity was observed for both K^+ -ISE and Na^+ -ISE.⁹ The low detection limits and the slope sensitivities of the K^+ -ISEs based on valinomycin are improved in the following order of the TPB derivatives: TPB<Cesibor<TCPB<TFPB. The order is in accord with the sequence of the lipophilicity of TPB derivatives. Imato *et al.*¹⁹ reported the effect of the kind of the ion-exchangers on the sensitivity of a PVC membrane based Vitamin B₁ ISEs using TPB derivatives as the ion-exchanger. They found that the low detection limits and the slope sensitivities of the Vitamin B₁ ISEs improve in the order of TPB<Cesibor<TCPB=TFPB and the order is the same as the increase in the lipophilicity of the ion-exchanger. The fact that the low detection limits and the slope sensitivities of the Vitamin B₁ ISEs improve in the order of TPB<Cesibor<TCPB=TFPB, may be the result of a decrease in the solubility of the TPB derivatives anions from the solvent polymeric sensing-membrane into the sample solution. In analogy with the Vitamin B₁ ISE, the fact that the low detection limit and the slope sensitivity of the K^+ -ISE based on valinomycin are improved appar-

Fig. 1 The K^+ response of valinomycin (a) and bis(benzo-15-crown-5) (b) based K^+ -ISEs based on various kinds of TPB derivatives.

ently in the order of TPB < Cesibor < TCPB < TFPB may be the effect of decreases in the solubility of the sensing-materials composed of complex salt between potassium cation and the neutral carrier and a counter anion, one of the TPB derivatives. In contrast, the low detection limits and the slope sensitivities of K^+ -ISEs based on B15C5 are improved in the following order of the TPB derivatives: TPB < Cesibor = TCPB = TFPB. The results of the response characteristics of valinomycin and B15C5 based K^+ -ISEs indicate that the kind of the neutral carrier also influences the response characteristics of K^+ -ISE. The effect of the kind of the neutral carrier on the response characteristics of the K^+ -ISE may be due to the difference of complex formation constants between neutral carriers and cations.²⁰

Response of K^+ - μ -ISFET and Na^+ - μ -ISFET based on various kinds of TPB derivatives

Figures 2 and 3 show the responses of the B15C5-based K^+ - μ -ISFETs and those of the B12C4-based Na^+ - μ -ISFETs with various kinds of TPB derivatives, respectively. In the case of both μ -ISFETs, the concentrations of TPB derivatives in the liquid membrane are 33 and 67 mol% of the neutral carrier. The low detection limits and the slope sensitivities of the K^+ - μ -ISFETs are improved in the following order of the TPB derivatives irrespective of the concentration of the neutral carrier: TPB < Cesibor = TFPB = TCPB. The result is similar to that of the response of the valinomycin based

K^+ - μ -ISFETs.¹⁸ The effect of the additive salts is observed not only in the K^+ - μ -ISFETs, but also in the Na^+ - μ -ISFETs. For the case of the Na^+ - μ -ISFETs, where the concentration of TPB derivatives in the liquid membrane are 33 and 67 mol%, the low detection limits and the slope sensitivities are improved in the following order of the TPB derivatives: TPB < Cesibor < TCPB = TFPB. The sensitivity characteristics, however, show some concentration dependence. The response characteristics of the Na^+ - μ -ISFET whose liquid membrane contains TPB derivatives of 67 mol% is worse than that of 33 mol%, especially in the case of Cesibor. The concentration dependence on sensing characteristics of the Na^+ - μ -ISFETs should be contrasted to those of valinomycin¹⁸ and B15C5 based K^+ - μ -ISFETs. Neither of K^+ - μ -ISFETs show no concentration dependence of sensitivities in this concentration range.

Effect of concentration of additive salts in response of K^+ - μ -ISFET and Na^+ - μ -ISFET

Figure 4 shows the effect of the concentration of the additive salts on the response characteristics of B15C5-based μ -ISFET using Cesibor as an additive salt. The μ -ISFET shows the Nernstian response to K^+ ion from 10^{-6} to 10^{-1} M in the case of B15C5-based liquid membrane for Cesibor concentration less than 90 mol%. On the other hand, the low detection limits and the slope sensitivities of B15C5-based μ -ISFETs are affected by

Fig. 2 The K^+ response of bis(benzo-15-crown-5) based K^+ -ISFET based on various kinds of TPB derivatives. Concentration of additive salt: (a) 33 mol%, (b) 67 mol%.

Fig. 3 The Na^+ response of bis(12-crown-4) based Na^+ -ISFET based on various kinds of TPB derivatives. Concentration of additive salt: (a) 33 mol%, (b) 67 mol%.

Fig. 4 The effect of the concentration of the additive salts on K^+ response of bis(benzo-15-crown-5) based K^+ -ISFETs using Cesibor as an additive salt.

Cesibor as its concentration increases to more than 100 mol%. We have already reported that the low detection limits and the slope sensitivities of μ -ISFETs are affected as the Cesibor concentration increases to more than 90 mol% in case of valinomycin-based liquid membrane.¹⁸ As described previously, the response characteristics of B12C4 based μ -ISFET in the concentration of TPB derivatives of 33 mol% is better than that of 67 mol%. This indicates that the concentration-dependent effect of additive salts in the response characteristics of the μ -ISFET depends on the kinds of the neutral carriers. The fact that the potassium and sodium response deteriorates as the Cesibor concentration increases might be explained as follows: As the concentration of anionic sites increases, non-complexed potassiums are exchanged simply at the anionic sites at liquid-liquid interface of sensing liquid membranes and the response of the μ -ISFETs approaches that of a dissociated ion-exchanger. The further study on the concentration-dependence mechanism is now under investigation. Shibata and Miyagi² found that the Na^+ selectivity of bis(crown ether) based Na^+ -ISE with TFPB as an additive salt is reduced as TFPB concentration increases. Bakker *et al.*²¹ also found that for dicyclohexyl-18-crown-6 based K^+ -ISE with TCPB as an additive salt, the selectivity of K^+ against the monovalent cations is reduced as TCPB concentration increases. These

results also support our data concerning the effect of the concentration of the additive salts on the response of μ -ISFET.

In this paper, we have evaluated the effect of additive salts on low detection limit and slope sensitivity in the response characteristics of K^+ and Na^+ -selective ISEs without the effect of anionic sites in PVC using μ -ISFETs for the first time. From our results, we found that the sensitivity of neutral-carrier based K^+ and Na^+ - μ -ISFETs depends on the kinds and the concentration of the additive salts.

References

1. W. E. Morf, G. Kahr and W. Simon, *Anal. Lett.*, **7**, 9 (1974).
2. Y. Shibata and H. Miyagi, *Nippon Kagaku Kaishi*, **1992**, 33.
3. T. A. Nieman and G. Horvai, *Anal. Chim. Acta*, **170**, 359 (1985).
4. E. Lindner, K. Tóth, E. Pungor, W. E. Morf and W. Simon, *Anal. Chem.*, **50**, 1627 (1978).
5. U. Schaller, E. Bakker, U. E. Spichiger and E. Pretsch, *Anal. Chem.*, **66**, 391 (1994).
6. E. Bakker, M. Naegle, U. Schaller, E. Bakker and E. Pretsch, *Anal. Chem.*, **67**, 3123 (1995).
7. R. Eugster, P. M. Gehrig, W. E. Morf, U. E. Spichiger and W. Simon, *Anal. Chem.*, **63**, 2285 (1991).
8. R. Eugster, U. E. Spichiger and W. Simon, *Anal. Chem.*, **65**, 689 (1993).
9. S. Wakida, K. Hayano, Y. Shibutani, K. Yakabe, T. Shono, S. Yoshikawa and K. Higashi, *Chem. Lett.*, **1994**, 2033.
10. G. Horvai, E. Gráf, K. Tóth, E. Pungor and R. P. Buck, *Anal. Chem.*, **58**, 2735 (1986).
11. K. Tóth, E. Gráf, G. Horvai, E. Pungor and R. P. Buck, *Anal. Chem.*, **58**, 2741 (1986).
12. R. P. Buck, K. Tóth, E. Gráf, G. Horvai and E. Pungor, *J. Electroanal. Chem. Interfacial Electrochem.*, **223**, 51 (1987).
13. A. Van den Berg, P. D. Van del Wal, M. Skowronska-Ptásinska, E. J. R. Sudhölter, D. N. Reinhoudt and P. Bergveld, *Anal. Chem.*, **59**, 2827 (1987).
14. E. Lindner, E. Gráf, Z. Niegreis, K. Tóth, E. Pungor and R. P. Buck, *Anal. Chem.*, **60**, 295 (1988).
15. M. L. Iglehart, R. P. Buck and E. Pungor, *Anal. Chem.*, **60**, 290 (1988).
16. T. Masadome, S. Wakida, Y. Kawabata, T. Imato and N. Ishibashi, *Anal. Sci.*, **8**, 89 (1992).
17. P. Bühlmann, S. Yajima, K. Tohda and Y. Umezawa, *Electrochim. Acta*, **40**, 3021 (1995).
18. T. Masadome, T. Tjang Kie, S. Wakida and K. Higashi, *Anal. Commun.*, **34**, 389 (1997).
19. G. H. Zhang, T. Imato, Y. Asano, T. Sonoda, H. Kobayashi and N. Ishibashi, *Anal. Chem.*, **62**, 1644 (1990).
20. E. Bakker, M. Willer, M. Lerchi, K. Seiler and E. Pretsch, *Anal. Chem.*, **66**, 516 (1994).
21. T. Rosatzin, E. Bakker, K. Suzuki and W. Simon, *Anal. Chim. Acta*, **280**, 197 (1993).

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