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Effects of Additive Salts on Electrochemical Characteristics of Neutral Carrier Based Electrodes

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Remarkable effects of such additive salts as tetraphenylborate derivatives on low detection limit and slope sensitivity were found in electrochemical characteristics of sodium-selective neutral carrier based electrodes by using bis(12-crown-4).

Recently, neutral carrier based ion-selective electrodes (ISEs) method has become widely used as routine analysis of Na^+ and K^+ in biological samples in clinical laboratories, since a number of studies on neutral carrier based ISEs have been carried out. The neutral carrier based sensing-membrane consists of neutral carrier, membrane solvent, membrane matrix and additive salt generally. As additive salt, sodium tetraphenylborate (Na TPB) and its more lipophilic analogue potassium tetrakis(4-chlorophenyl)borate (K TCPB) are used commonly.

These additive salts have been reported to effect electrochemical characteristics of ISEs as follows; reduction or elimination of interfering lipophilic anions,[1] reduction of the electrical membrane resistance,[2] reduction of the electrode response time[3] and improvement of selectivity in lithium ISEs.[4]

However, a systematic study has not carried out on such additive salts as tetraphenylborate derivatives on low detection limit and slope sensitivity in electrochemical characteristics of neutral carrier based ISEs. In this paper, we will describe remarkable effects of the additive salts, as shown in Fig. 1, on electrochemical characteristics of sodium-selective electrodes by using bis(12-crown-4).

The neutral carrier based Na^+-sensitive membrane was prepared by casting the corresponding tetrahydrofuran solution, which consists of 10 mg of bis(12-crown-4), 200 mg of 2-nitrophenyloctylether, 100 mg of PVC and 5 mg of each TPB derivatives, onto the tip of ISE's kit (DKK Corp.). After conditioning, the potential responses were measured in the following electrochemical cell; Ag/AgCl, *satd.* KCl | 0.1 mol dm^{-3}

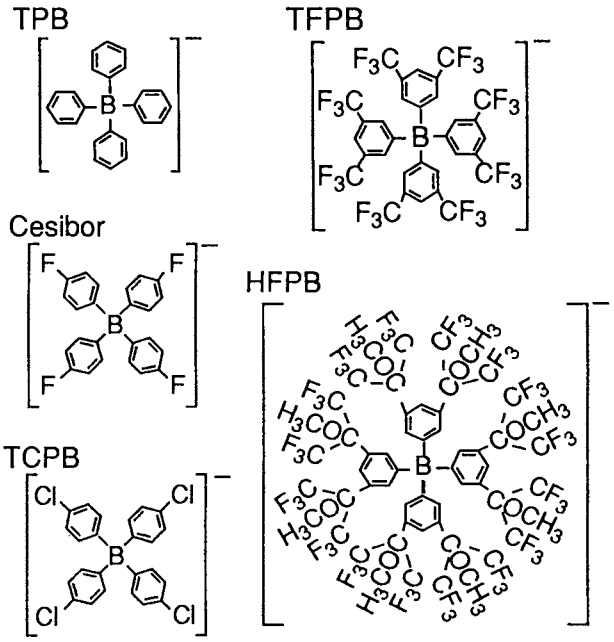

Fig. 1. Chemical structures of TPB derivatives.

CH_3COOLi | sample | membrane | 0.01 mol dm^{-3} NaCl, AgCl-Ag_2S/Ag.

Calibration curves of Na^+-ISEs based on various kinds of TPB derivatives are shown in Fig. 2. This figure shows remarkable effects of additive salts on low detection limit as well as slope sensitivity. The low detection limits of Na^+-ISEs are improved in the order of the following TPB derivatives;

HFPB ≒ TFPB > TCPB > Cesibor > TPB.

The slope sensitivity of Na^+-ISEs also increase in the order of

HFPB ≒ TFPB ≒ TCPB > Cesibor > TPB.

The order seems to be considerably similar to that of lipophilicity of TPB derivatives except for HFPB.

Imato *et al.* reported the order of sensitivity of ion-exchanger based Vitamin B1 electrode by using various ion-exchangers such as TPB derivatives, dipicrylaminate and dinonylnaphthalenesulfonate.[5] Among TPB derivatives, the sensitivity for low concentrations in the Vitamin B1 electrodes increases in the order of

HFPB > TFPB ≒ TCPB > Cesibor > TPB.

The order of the Vitamin B1 electrode seems to be fairly similar to that of lipophilicity of TPB derivatives.

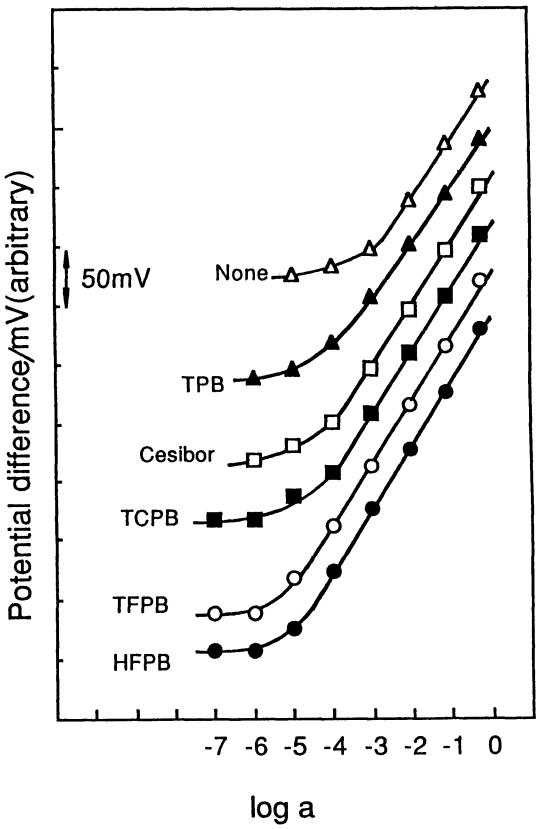

Fig. 2. Calibration curves of Na^+-ISEs based on various kinds of TPB derivatives.

In case of ion-exchanger based ISEs, the order may be brought about by the decrease of solubility of the ion-exchangers from the solvent polymeric sensing-membrane into the sample solution, which ion-exchangers are sensing materials composed of Vitamin B1 cation and one of the TPB derivatives anions. In the same manner, in case of neutral carrier based ISEs, the order could be brought about by the decrease of solubility of the sensing-materials composed of sodium cation, neutral carrier and one of the TPB derivatives anions, however, it is difficult to discuss the results from our few data because the order of the Na^+-ISE with HFPB doesn't follow that of lipophilicity of TPB derivatives. The similar effects were also found in K^+-ISEs by using valinomycin. These phenomena appear to be an important observation for the response mechanism of ISEs. Further studies are currently being investigated.

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