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ION-SELECTIVE ELECTRODES RESPONSIVE TO MALEIC AND PHTHALIC ACIDS

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The electrode membranes responsive to maleic and phthalic acids were prepared by using the organic solvent solutions of the crystal violet salts of the corresponding organic anions. The responses of both the electrodes are linear down to 10^{-4} - $10^{-4.5}$ M, with an ideal Nernstian slope of 58 mV per activity decade at 20 °C.

Maleic acid is easily extracted into an organic solvent, forming an ion pair with a large cation such as crystal violet ion, whereas the trans-isomer, fumaric acid, is not extracted. A similar phenomenon is observed among the aromatic dicarboxylic acids, such as phthalic, isophthalic and terephthalic acids, and the o-isomer is preferentially extracted. Noting the differences of the extractabilities among the isomers, we have prepared the electrode membranes which selectively respond to the cis- or o-isomer of the organic acids, and studied their analytical behavior.

The liquid membrane was the 10^{-4} M organic solvent solution of the crystal violet salt of the corresponding monovalent organic anion, and was prepared by a solvent extraction method.[1] Nitrobenzene(NB), 1, 2-dichloroethane(DCE) and chloroform(CF) were used as solvents. The potential measurement of the following electrochemical cell was made by a Takeda Riken Electrometer TR 8651.

+ SCE/ Reference Solution/ Liquid Membrane/ Sample Solution/ SCE -

Table 1. Summary of behavior of carboxylate ion-selective electrodes at 20 °C

Electrode	Solvent	Slope (mV/log a)	Lower limit of linear response (M)	Selectivity coefficient
Maleic acid	NB	-58	10^{-4}	trans-isomer 0.001, CF_3COO^- 0.4, Salicylic acid 5.6, Cl^- 0.002, Phthalic acid 6.7, Benzoic acid 0.02
	DCE	-58	10^{-4}	trans-isomer 0.001, CF_3COO^- 0.3, Salicylic acid 4.2, Cl^- 0.004, Phthalic acid 5.2, Benzoic acid 0.03,
	CF	-58	10^{-4}	trans-isomer 0.001, CF_3COO^- 0.08, Salicylic acid 1.5, Cl^- 0.006, Phthalic acid 3.6, Benzoic acid 0.01,
Phthalic acid	NB	-58	$10^{-4.5}$	m- and p-isomers 0.01, CF_3COO^- 0.06, Maleic acid 0.15, Salicylic acid 0.85, Cl^- 0.0003, Benzoic acid 0.003,
	DCE	-58	$10^{-4.5}$	m- and p-isomers 0.01, CF_3COO^- 0.06, Maleic acid 0.19, Salicylic acid 0.81, Cl^- 0.0008, Benzoic acid 0.005,
	CF	-58	10^{-4}	m- and p-isomers 0.01, CF_3COO^- 0.02, Maleic acid 0.28, Salicylic acid 0.42, Cl^- 0.001, Benzoic acid 0.003,

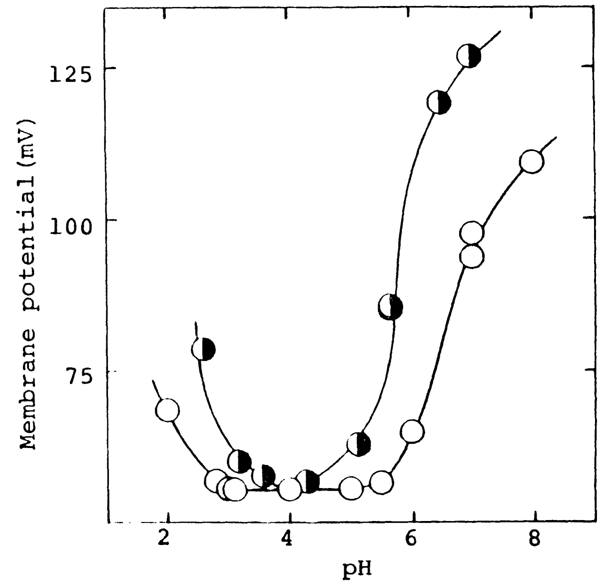

Fig. 1 Influence of pH on electrode potential
○ hydrogenmaleate electrode
◑ hydrogenphthalate electrode
sample solution: 10^{-3} M solution of corresponding organic acid with a varing pH

The set-up of the cell and the procedure of the potential measurement were described in detail in a previous paper.[2] The reference solution was the 10^{-2} M aqueous solution of the corresponding organic acids, and its pH was maintained at 4. The pH of the sample solution was adjusted within the range 3 to 5 and 3.8 to 4.2 for maleic and phthalic acids, respectively. In these pH ranges, the organic acids exist as the monovalent anion species.

The response manner, the sensitivity and the selectivity are summarized in Table 1. The selectivity coefficients are the values for the monovalent foreign anions, and were determined by the separate solution method.[3] The responses of both the electrodes are linear down to 10^{-4} - $10^{-4.5}$M, with an ideal Nernstian slope of 58 mV per activity decade at 20 °C, suggesting that the electrodes are monovalent anion-responsive. Fig. 1 shows the influence of the pH on the membrane potential. The potential varies in accordance with the distribution of the monovalent anion which is a function of pH; accordingly the interferences of corresponding divalent anions of the organic acids are extremely low. In practical use of the electrodes, the pH of the sample solution must be kept within the range mentioned above.

The electrode responsive to maleic acid works well without interference of the trans-isomer, and that responsive to phthalic acid is not interfered from the m- or p-isomer of phthalic acid.

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