# Ion-selective Electrode Membranes Responsive to Maleic and Phthalic Acids

Akinori Jyo, Morihisa Yonemitsu, and Nobuhiko Ishibashi*

*Department of Applied Analytical Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812*

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Ion-selective electrodes responsive to maleic and phthalic acids were prepared. The organic solvent solution of the ion-pair of the objective monovalent acid anion with a Crystal Violet or a tris(bathophenanthroline)-iron(II) ion was used as the electrode membrane. The responses of both electrodes were linear down to $10^{-4}$—$10^{-4.5}$ M, with an ideal Nernstian slope of 57—58 mV per activity decade at 20 °C. Together with the potential slope, the pH dependence of the potential showed that the electrode responded to the monovalent anion of maleic or phthalic acid. The interferences of acetate, benzoate, and chloride were extremely low, whereas iodide and perchlorate interfered greatly. The maleic acid electrode works well without the interference of fumaric aicd. The phthalic acid electrode also functions without any interferences by isophthalic or terephthalic acid.

Various methods of analyzing maleic and phthalic acids have been reported.[1–6] However, no report has been presented on an electrode responsive to maleic or phthalic acid.

Maleic acid is easily extracted into an organic solvent containing a large cation, such as a crystal violet or a tris(bathophenanthroline)iron(II) ion, and forms an ion-pair with the cation, whereas fumaric acid, the *trans*-isomer of maleic acid, is not extracted. A similar phenomenon is observed among the isomers of the benzenedicarboxylic acids, and phthalic acid is preferentially extracted into the above-mentioned organic solvent from an aqueous solution of a mixture of the isomers.

In a previous communication, we have briefly reported on the performances of maleic acid- and phthalic acid-sensitive electrodes prepared by utilizing the extractability differences among the isomers.[7] This paper will describe further details of the preparations and performances of the electrodes. By using the electrodes, it became possible to determine the concentrations of the acids more rapidly and simply than by the conventional methods.

## Experimental

*Reagents.* All the chemicals used were of reagent-grade quality. The aqueous solution of the monosodium salt of maleic or phthalic acid was prepared by mixing the aqueous solution of the acid and the sodium hydroxide solution in an appropriate ratio. The pH of the sample solution was adjusted with an aqueous solution of sulfuric acid, potassium dihydrogenphosphate, or sodium hydroxide.

*Sensitive Liquid Membrane.* An organic solvent solution of the Crystal Violet salt or the tris(bathophenanthroline)iron(II) salt of the objective monovalent acid anion was used as the liquid membrane. The concentration of the salt was $10^{-4}$ M. Nitrobenzene (NB), 1,2-dichloroethane (DCE), and chloroform (CF) were used as the solvents of the membrane.

The membrane solution containing the crystal violet salt was prepared by the following solvent extraction method. Equal volume portions of the organic solvent, a $10^{-2}$ M aqueous solution of the acid, and a $10^{-3}$ M aqueous solution of Crystal Violet were poured into a separating funnel, after which the funnel was shaken with a mechanical shaker for 30 min. After the separation of layers, the organic phase was shaken again with a $10^{-3}$ M aqueous solution of the acid in order to purify it. In the extraction process, the pH of the aqueous phase was maintained at 4 in order to extract the acid as a monovalent anion. The organic phase was separated and diluted with the organic solvent saturated with water. The organic solution thus obtained was used as the sensitive membrane. The membrane solution which contained the tris(bathophenanthroline)iron(II) salt was prepared by a similar procedure.

*Potential Measurement.* The potential of the following electrochemical cell was measured by using a Takeda Riken Electrometer TR 8651.

+SCE|Reference Solution|Liquid Membrane|Sample Solution|SCE−

The cell assembly has been illustrated in detail elsewhere.[8] The lower part of a glass U-tube was filled with 10 ml of the membrane solution, the reference and sample solutions, 10 ml of each, were thus separated. An agar salt bridge saturated with potassium chloride or ammonium chloride was used to connect the respective saturated calomel electrode (SCE) with the reference and sample solutions. The reference solution was a $10^{-2}$ M aqueous solution of the objective organic acid, its acidity has been adjusted to pH 4.

## Results and Discussion

*Potential Response of the Electrode.* In the potentiometric determination of the concentration of maleic or phthalic acid, an electrode responsive to a monovalent anion, *i.e.*, a hydrogenmaleate or hydrogenphthalate ion, is preferable to a divalent maleate ion- or phthalate ion-responsive electrode from an analytical viewpoint, because the slope of the calibration curve of the former electrode can be expected to be twice that of the latter electrode.

Since the first and second dissociation constants are $10^{-1.92}$ and $10^{-6.22}$ for maleic acid, and $10^{-2.95}$ and $10^{-5.41}$ for phthalic acid, respectively, the main component species of the acids are the monovalent anions around pH 4. Accordingly, the response of the electrode was examined on the sample solution at pH 4

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* To whom any correspondence should be addressed.

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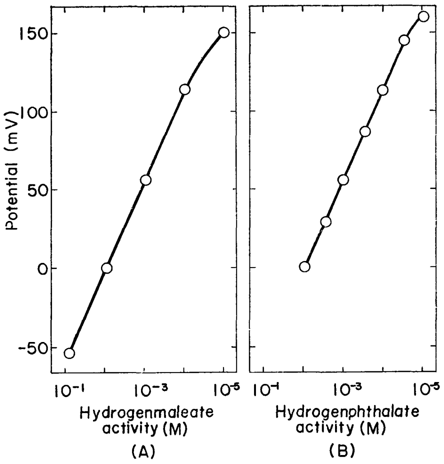

Fig. 1. Responses of maleic acid electrode(A) and phthalic acid electrode(B).

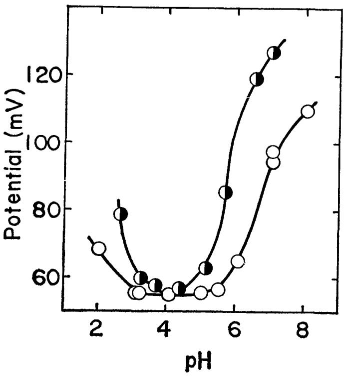

Fig. 2. Influence of pH on electrode potential.
Phthalic acid electrode (◑)
Maleic acid electrode (○)
Membrane: $10^{-4}$ M nitrobenzene solution of crystal violet salt of corresponding monovalent acid anion.

in order to detect the acid as monovalent anion species.

Figure 1 shows the potential response of the electrode. The membrane consisted of a $10^{-4}$ M nitrobenzene solution of the crystal violet salt of the monovalent acid anion. The response of the phthalic acid electrode could be examined on the sample solution below $10^{-2}$ M because of the small solubility of phthalic acid at pH 4. The activity coefficient of the objective anion was calculated from the Debye-Hückel equation, in which the ion-size parameter was assumed to be equal to those of salicylate and vinylacetate.[9] The responses of both electrodes were linear over the activity ranges from $10^{-1}$ to $10^{-4}$ M and from $10^{-2}$ to $10^{-4.5}$ M for the maleic and phthalic acid sample solutions respectively. An ideal Nernstian slope of 58 mV per activity decade at 20 °C was observed for each electrode. Equilibrium potentials were achieved within a few sec, and potential values were reproducible to ±0.2 mV.

The responses of the electrodes with different ion-exchange sites and different membrane solvent species are summarized in Table 1. Irrespective of the site and the membrane solvent species, the properties of the electrode membranes, such as the potential slope, the response time, and the stability of the potential, were almost the same as those of the nitrobenzene membranes described above. The slope of 57—58 mV indicated that the electrodes responded to the monovalent anion species of maleic and phthalic acids.

*Influence of pH on the Electrode Potential.* The potential can be effected to vary with the pH of the sample solution, since the relative concentration of the monovalent anion depends on the acidity of the solution. Figure 2 shows the potentials of the electrodes for $10^{-3}$ M sample solutions with different pH values. The theoretical value of 56 mV was observed in the pH ranges from 3 to 5 and from 3.8 to 4.2 for the solutions of the maleic and phthalic acids respectively. In the higher and lower pH regions, the remarkable change in the potential was in accordance with the concentration decrease in the monovalent anion species of the acid. This suggests that the electrodes

TABLE 1. RESPONSES OF ELECTRODES AT 20 °C

| Electrode | Site | Solvent | Slope (mV/log *a*) | Lower limit of linear response (M) |
|---|---|---|---|---|
| Maleic acid | $\mathrm{CV^+}$ [a] | NB | −58 | $10^{-4}$ |
| | | DCE | −58 | $10^{-4}$ |
| | | CF | −58 | $10^{-4}$ |
| | Fe (B·phen)$_3^{2+}$ [a] | NB | −57 | $10^{-4}$ |
| | | DCE | −57 | $10^{-4}$ |
| | | CF | −57 | $10^{-4}$ |
| Phthalic acid | $\mathrm{CV^+}$ | NB | −58 | $10^{-4.5}$ |
| | | DCE | −58 | $10^{-4.5}$ |
| | | CF | −58 | $10^{-4}$ |
| | Fe(B·phen)$_3^{2+}$ | NB | −57 | $10^{-4}$ |
| | | DCE | −57 | $10^{-4}$ |
| | | CF | −57 | $10^{-4}$ |

a) $\mathrm{CV^+}$ and Fe(B·phen)$_3^{2+}$ denote Crystal Violet and tris(bathophenanthroline)iron(II) ions, respectively.

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[9] J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

TABLE 2. INFLUENCES OF COEXISTING ISOMERS ON ELECTRODE POTENTIAL

| Electrode | Interferant ($j$) | Concn. of interferant (M) | Slope (mV/log $a$) | Lower limit of linear response (M) |
|---|---|---|---|---|
| Maleic acid | Fumaric acid | $1.0\times10^{-2}$ | $-57$—$-58$ | $10^{-4}$ |
| Phthalic acid | Isophthalic acid | $2.0\times10^{-3}$ | $-57$—$-58$ | $10^{-4}$—$10^{-4.5}$ |
| | Terephthalic acid | satd. ($\simeq10^{-4}$) | $-57$—$-58$ | $10^{-4}$—$10^{-4.5}$ |

TABLE 3. SELECTIVITY COEFFICIENTS OF MALEIC ACID ELECTRODE AT 20 °C

| Interferant | Membrane | | | | |
|---|---|---|---|---|---|
| (Site) | $CV^+$ | | | $Fe(B\cdot phen)_3^{2+}$ | |
| (Solvent) | NB | DCE | CF | NB | DEC |
| Acetic acid | — | 0.0001 | — | — | — |
| Fumaric acid | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| Benzoic acid | 0.02 | 0.03 | 0.01 | — | — |
| $CF_3COO^-$ | 0.4 | 0.3 | 0.08 | — | 0.3 |
| Salicylic acid | 5.6 | 4.2 | 1.5 | 5.7 | — |
| Phthalic acid | 6.7 | 5.2 | 3.6 | 7.0 | 5.3 |
| Benzilic acid | 10 | 10 | 3.7 | — | — |
| $Cl^-$ | 0.002 | 0.004 | 0.006 | — | — |
| $Br^-$ | — | 0.09 | — | — | — |
| $NO_3^-$ | 0.7 | 0.6 | — | — | — |
| $I^-$ | 15 | 14 | 7 | — | — |
| $ClO_4^-$ | $1.1\times10^3$ | $6.0\times10^2$ | 16 | $1.1\times10^3$ | $5.3\times10^2$ |

TABLE 4. SELECTIVITY COEFFICIENTS OF PHTHALIC ACID ELECTRODE AT 20 °C

| Interferant | Membrane | | | | |
|---|---|---|---|---|---|
| (Site) | $CV^+$ | | | $Fe(B\cdot phen)_3^{2+}$ | |
| (Membrane) | NB | DCE | CF | NB | DEC |
| Acetic acid | — | $2\times10^{-5}$ | — | — | — |
| *p*- and *m*-isomer | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Benzoic acid | 0.003 | 0.005 | 0.003 | 0.003 | 0.005 |
| $CF_3COO^-$ | 0.06 | 0.06 | 0.02 | — | 0.05 |
| Maleic acid | 0.15 | 0.19 | 0.28 | 0.14 | 0.19 |
| Salicylic acid | 0.85 | 0.85 | 0.42 | — | — |
| Benzilic acid | 1.5 | 2 | 0.9 | — | — |
| $Cl^-$ | 0.0003 | 0.0008 | 0.001 | — | — |
| $Br^-$ | — | 0.02 | — | — | — |
| $NO_3^-$ | 0.1 | 0.1 | — | — | — |
| $I^-$ | 2 | 3 | 2 | — | — |
| $ClO_4^-$ | $1.4\times10^2$ | $1.2\times10^2$ | 4 | $1.4\times10^2$ | $1.0\times10^2$ |

do not respond to the undissociated acids and the divalent anions of the acids, and supports the view that the acids are extracted into an organic solvent as monovalent anions and not as divalent anions.[6] In the practical use of the electrode, care must be taken in the adjustment of the pH of the sample solution.

*Selectivity of the Electrode.* The potential, $E$, for the sample solution containing the primary ion, i, and any other ion, j, is given by the empirical Eq. (1):

$$E = 2.303\,RT/F\log(a_i'/(a_i''+Ka_j'')) \qquad (1)$$

where $a_i$ and $a_j$ are the activities of the monovalent anions, i and j, and where $K$ is a selectivity coefficient. The activities of the reference and sample solutions are designated by prime and double prime respectively.

The interfering effects of the isomer ions were examined on the basis of the mixed solution method.[10] In this method, the potential was measured on a series of sample solutions, each solution containing a fixed amount of an interferant, j, and a varying amount of the primary ion, i. The influences of the isomer ions are summarized in Table 2. At the lowest limit of linear response, the sample solution contained 100 times more fumaric acid than maleic acid, and about 20 times more isophthalic acid than phthalic acid.

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[10] G. J. Moody and J. D. R. Thomas, "Selective Ion Sensitive Electrodes," Merrow Pub. Co. Watford, England, (1972).

However, no interfering effect of fumaric or isophthalic acid was observed. The response of the phthalic acid electrode was not affected by the presence of the terephthalic acid, even in the saturated solution of the latter acid. These results indicate that the electrodes are capable of determining the concentrations of maleic and phthalic acids without any interference by the isomer acids.

The interfering effects of other organic and inorganic anions were examined by using the separate-solution method.[10] In this method, the potential was measured on the sample solution containing an interferant alone. The pH of the sample solution was maintained within the region where the interferant existed as a monovalent anion. In Table 3, the selectivity coefficients of the maleic acid electrode are listed. The interferences of acetate, benzoate, and chloride were extremely low, but the salicylate and iodide interfered greatly. The perchlorate ion showed the highest interference. The selectivity of the phthalic acid electrode is also summarized in Table 4. The selectivity of the phthalic acid electrode was better than that of the maleic acid electrode. The chloroform membrane electrode had slightly higher selectivity values than the nitrobenzene and 1,2-dichloroethane membrane electrodes. The selectivity coefficients were approximately independent of the site species if the electrode membrane was prepared by using the same solvent with a relatively high dielectric constant. These results agree with the view proposed by Eisenman of the selectivity of the ion-sensitive electrode with a liquid ion-exchanger membrane of the complete-dissociation type.[11]

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11) G. Eisenman, *Anal. Chem.*, **40**, 310 (1968).