Methanol, N, N-dimethylformamide 및 Acetonitrile 속에서 유리전극의 pH 응답성

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The Response Characteristic of Hydrogen-responsive Glass Electrode in Methanol, N, N-dimethylformamide and Acetonitrile

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요 약 : 메타놀, N, N-디메칠포름아미드 및 아세토니트릴 속에서 유리전극의 pH 응답성을 여러가지 pH의 완충용액으로 시험한바 전극을 물속에 보관하는 것보다 측정하고저 하는 용매속에 보관하는 것이 더 빨리 전위가 안정되었다. 같은 용매에서 용액의 염기성에 비례하여 응답속도가 느리고 강염기성 용액에서는 안정한 전위를 얻기 어려웠다. 산성용액에서의 pH 응답성은 보다 빠르나 같은 용액의 pH 측정에서도 전극의 사용한 이력에 따라 응답성과 측정치에 차이가 생겼다.

Abstract The responsive characteristics of hydrogen-responsive glass electrode in various buffer solutions of methanol, N, N-dimethylformamide and acetonitrile were examined. The potentials were attained more rapidly with an electrode stored in the same solvent medium than that stored in water before use. However, the time to be required for a stable potential increased with the basicity of buffer solution, and it was not provide a consatnt potential in the strong basic solution of these solvent. Even in acidic solution, the potential was varied according to the past usage of the electrode.

Introduction

In nonaqueous solution, the hydrogen-responsive glass electrode has been used for determination of pH values and succesful in titrimetry. However, the time response and reproduciblity of the glass electrode in nonaqueous solution are less favorable than those in aqueous solution. In order to attain a stable potential rapidly in most of potentiometric studies with the glass electrode in the nonaqueous solution, the glass electrode was filled with the same solvent medium on the inside as on the outside[1-5], or mercury as an internal filling[6]. These results are, however, thought to be in disagreement with the mechanism of the glass electrode to generate electromotive force, and hence it was confirmed that some change of internal filling had little or no effect on the time response[7]. Juillard measured the rate of response of commercial electrodes in

DMF, and reported that it obeyed first-order kinetics. Recently[5,9], in nonaqueous measurement the glass electrode was stored in either the same pure solvent or in the same solvent containing a little amount of tetraethylammonium salt or an acid, such as picric acid, before tests were commenced. The results of these treatments seemed to be satisfactory when the electrode was used in an acidic and neutral solution, but in a basic solution the behavior of it was quite different.

In this study, the time response and reproducibility of the glass electrode, which had been treated with the same solvent under various conditions before measurement, in the wide range of pH was examined.

Experimental

Solvent. DMF Nakarai (Japan) reagent grade N, N-dimethylformamide (DMF) was shaken with potassium hydroxide pellets[10] (30g/L. solvent) for two hours, decanted, and shaken with phosphorous pentoxide[11] (20~30 g/L. solvent) for two hours. After decanting the solvent was distilled at 50~60°C under reduced pressure through a distillator equipped with an adiabatic column of 650 mm long and 25 mm $i. d.$ packed with stainless steel wool. A fraction of about 70% was collected. The concentration of basic impurities in the freshly purified solvent as estimated spectrophotometrically at 400 mμ upon addition of p-nitrophenol was approximately $1 \times 10^{-5}M$, the water content by Karl Fisher titration was $\leq 0.01\%$ and the specific conductance was 7×10^{-8} $ohm^{-1}cm^{-1}$.

Methanol Pure reagent grade methanol was refluxed with barium oxide powder (20g/L. solvent) for two hours, and distilled at atmospheric pressure through the same distillator as described above. The water content was $\leq 0.005\%$ and the specific conductance was $5\sim10^{-8}$ ohm^{-1} cm^{-1}.

Acetonitrile Pure reagent grade acetonitrile (AN) was purified as following procedure[12,13]. 800 ml of AN was placed in a 1-liter round-bottom flask and added 10g of unhydrous sodium carbonate and 15 g of dried potassium permanganate, and was distilled at 5 to 10 ml/min. The distillate was made slightly acidic with concentrated sulfuric acid, and after the solvent had been decanted from the precipitated ammonium sulfate it was distilled at 10 to 20ml/hr. through the same distillator as described. Then the distillate was shaken with phosphorous pentoxide (20 g/L. solvent) and distilled. The resulting solvent had a specific conductance of $5\sim12\times10^{-8}$ ohm^{-1} cm^{-1} and the water content was $\leq0.003\%$.

Buffer solutions: Buffer solutions were made with different acids and their tetraethylammonium salts. Acids were employed with pure reagent grade. Tetraethylammonium salts were prepared by neutralizing the corresponding acid with a 10% tetraethylammonium hydroxide solution after the acid was dissolved in ethanol. The resulting solutions were evaporated to a syrupy state in a rotary evaporator. The products were twice azeotropically distilled with dry benzene and recrystallized from a benzene-DMF mixture except for the acetate, which was done from a benzene-ethanol mixture. They were dried at 50~70°C for 24 hours under reduced pressure. The concentration of these salt solutions were determined by means of nonaqueous potentiometric titration with picric or perchloric acid, and that of acid were determined with the aqueous standard solution of sodium hydroxide using phenolphthalein as an indicator.

Potentiometry A Yanagimoto Model pH-7 pH meter with a millivolt scale was used. When the potential was over the range of scale, the pH meter was connected with a conventional bias. A Horiba 1076 glass electrode was etched

in a 20% aqueous solution of ammonium bifluoride for 3 min., and stored in water over a week before use.

The reference half cell was an aqueous saturated calomel electrode(S. C. E.) with the same salt bridge as that used by Takaoka[14] in DMF. In methanol, a methanolic S. C. E. served as the reference electrode. In AN it was a Ag/AgClO₄ (0.005 M) electrode in AN containing 0.01M tetraethylammonium perchlorate(TEAP)

The cell for measurement of the E. M. F. was an H-type cell. The tip of the reference half cell was dipped into the compartment containing 0.05 M TEAP solution, and the other compartment was dipped with the glass electrode and filled with the buffer solution.

Tratment of the glass electrode When potentiometric measurements were made with a glass electrode stored in water, it was wiped with dry filter paper and dipped in the same solvent for 30 min., then it was rinsed with aceton and dried before measurement. After each measurement the electrode was dipped in 1 N aqueous hydrochloric solution for 5 hours, then stored in water over 12 hours before next measurement. In the case of mesurement with the glass electrode stored in the same solvent it had been stored in the same solvent containing 0.001 M picric acid over a week before use and when not in use it was kept in this solution.

All measurements were carried out under a nitrogen atmosphere at 25±1°C.

Results and Discussion

Fig. 1~*Fig.* 6 show the potential-time transient curves in various buffer solutions of these solvents. The time response of the glass electrode kept in the same solvent was more favorable than that of the electrode kept in water. The time, which was measured with the electrode treated with the same procedure, required to attain a stable potential was sample in order of methanol, AN and DMF. In the same solvent, the more basic the buffer solution, the more ample time was required. The potential of the electrode kept in water in the basic solution decreased with the time at first, but it reached a minimum at 15~30 min. and increased again in the curve. The time response measured with other commercial glass electrodes such as Horiba 1076 for alkali solution and Horda 1076-05T for high tempeature, are simillar as those shown in *Fig.* 1~6.
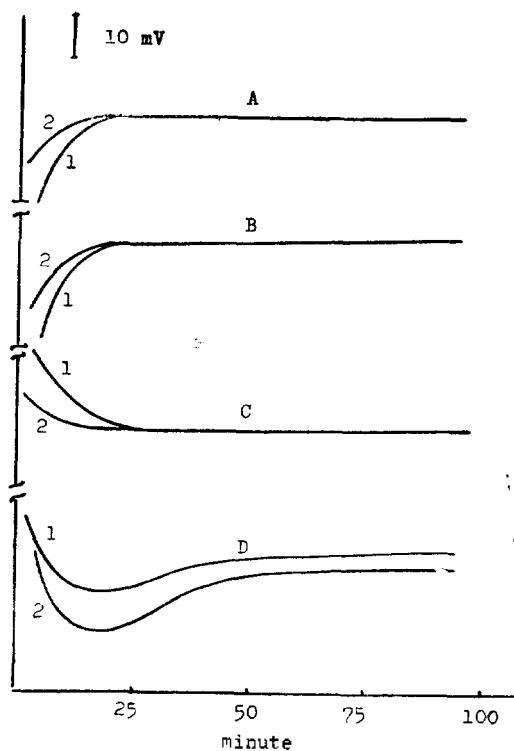

Fig. 1   Potential-time transient curves in methanol.
  1; the electrode stored in water
  2; stored in methanol
  A; 5 mM picric acid-5 mM TEA-picrate (pH=3.4)
  B; 5 mM salicylic acid-5 mM TEA-salicylate (7.7)
  C; 5 mM benzoic acid-5 mM TEA-benzoate (9.4)
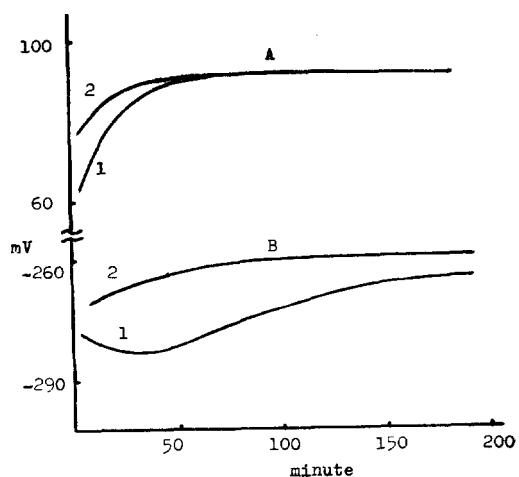 D; 5 mM TEA-bioxalate-5 mM TEA-oxalate (10.0)

Fig. 2 Potential-time transient curves in AN.
1; the electrode stored in water
2; the electrode stored in AN
A; 5 mM picric acid-5 mM TEA-Picrate
(pH=11. 0)
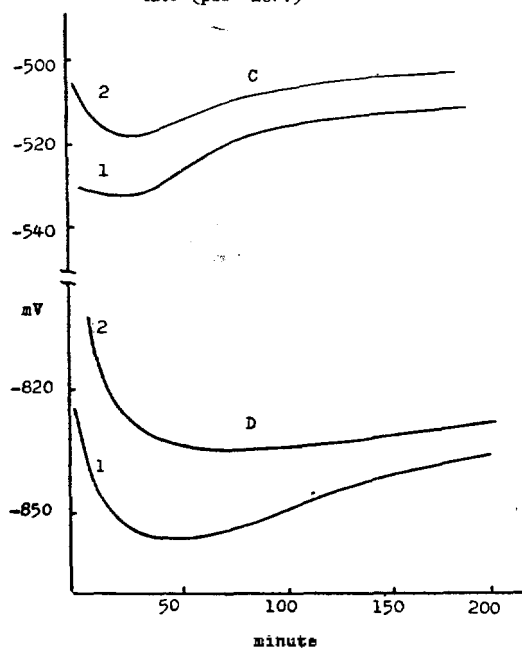B; 5 mM salicylic acid-5 mM TEA-salicy-
late (pH=16. 7)

Fig. 3 Potential-time transient curves in AN
1; the electrode stored in water
2; the electrode stored in An
C; 5 mM benzoic acid-5 mM TEA-benzoate
(pH=20. 7)
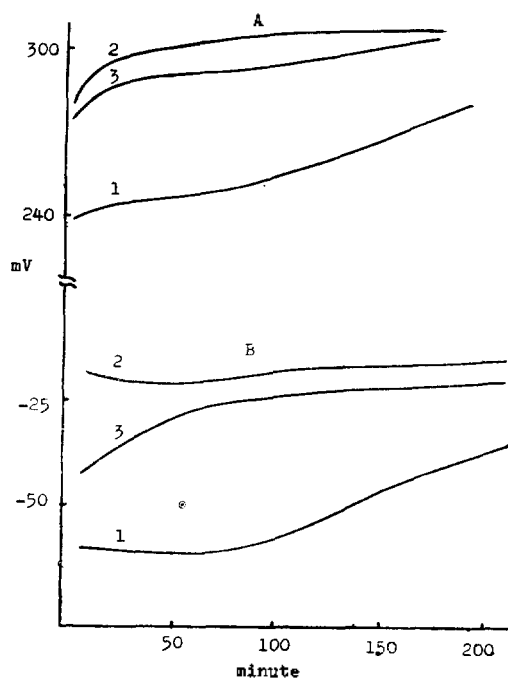D; 5 mM TEA-bioxalate-5 mM TEA-oxa-
late (pH=25. 3)

Fig. 4 Potential-time transient curves in DMF.
curve 3; with the electrode dipped in DMF
for 24 hrs. before measurement, the others
are the same as in fig. 1.
A; 5 mM picric acid-5 mM TEA-picrate
(pH=2. 4)
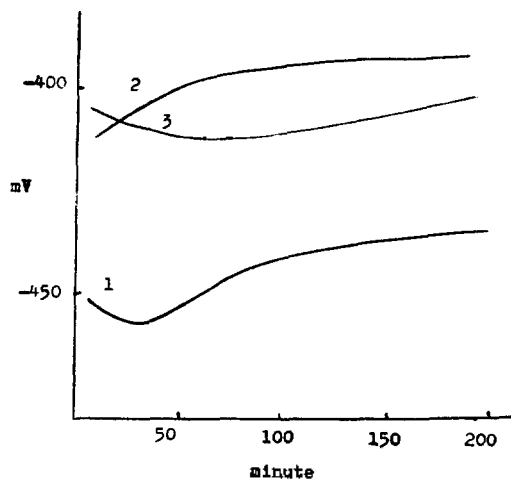B; 5 mM salicylic acid-5 mM TEA-Salicy-
late (pH=8. 2)

Fig. 5 Potential-time transient curves in DMF.
Buffer; acetate-acetic acid (pH=14. 0)
Curve 1; with the electrode stored in water
Curve 2; stored in DMF
Curve 3; with the electrode dipped in DMF
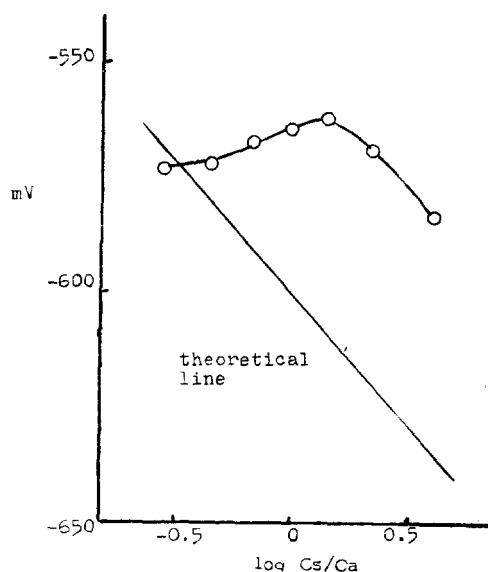for 24 hrs. before measurement.

Fig. 6 Potential-time transient curves in DMF.
　　　Buffer; oxalate-bioxalate (pH=17.2)
　　　Curve 1; with the electrode stored in water,
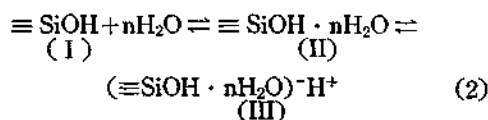　　　　　　measured three times.
　　　Curve 2; stored in DMF.

Many explanations have been given in regard to the mechanism of the E. M. F. generation of the glass electrode depending on hydrogen ion activity, and recently from a few experimental results [16] it is more prevalent theory that the E. M. F. response is explained in terms of diffusion potential at interfase which consist of the gel layer of the electrode and solution. The E. M. F. of the electrode connected with pH of aqueous solution is expressed as follows:

$$E = \frac{1}{F}(\mu_{H^+}^0 - \mu_{H^+}^{0'} - RT \ln a_{H^+}^s - 2.303$$

$$RT \cdot pH) \qquad (1)$$

where $\mu_{H^+}^0$ and $\mu_{H^+}^{0'}$ are the standard chemical potential of proton in solution and in gel layer; $a_{H^+}^s$ is the activity of proton in gel layer; R, T and F are the gas constant, absolute temperature and the Faraday, respectively and the other symbols are employed in their significances. As long as the $a_{H^+}^s$ in the gel layer, which is in
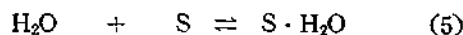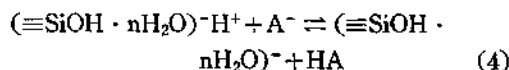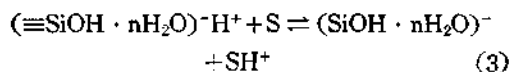
contact with the solution of pH in the range of weak acid to weak base, remains constant, the E. M. F. is directly proportonal to the pH. The presence of water in gel layer is necessary for liberation of proton.

However, no explanation has been given for the fact that the $a_{H^+}^s$ remains constant in spite of the diffusion of proton toward solution and transport of proton not occurs through the glass membrane. For the explanation of the $a_{H^+}^s$ to remain constsant, it is resonable to presume following equilibrium being established in the gel layer.

$$\equiv SiOH + nH_2O \rightleftharpoons \equiv SiOH \cdot nH_2O \rightleftharpoons$$
$$(\,I\,) \qquad\qquad (II)$$
$$(\equiv SiOH \cdot nH_2O)^- H^+ \qquad (2)$$
$$(III)$$

Taking acount of the basicity of silicate ion and the fact that ionic exchange on the gel layer scarcely occures in neutral solution, it can be thought that most of hydrated silicate sites present as uncharged form (II), and a small part of them ionizes (Form (III)) and is dehydrated (Form (I)). Though a part of proton diffuses toward solution, it can be supplied from the bulk of uncharged silicic acid, and for the constancy of the $a_{H^+}^s$ the activity of water in the gel layer, $a_{H_2O}^s$, is necessary to remain constant.

When the glass electrode which has been kept in water is in contact with nonaqueous solution contain-ing a basic anion for potentiometric pH measurement, the follwing equilibrium can be established at the interface of gel layer and

$$(\equiv SiOH \cdot nH_2O)^- H^+ + S \rightleftharpoons (SiOH \cdot nH_2O)^- + SH^+ \qquad (3)$$

$$(\equiv SiOH \cdot nH_2O)^- H^+ + A^- \rightleftharpoons (\equiv SiOH \cdot nH_2O)^- + HA \qquad (4)$$

$$H_2O \quad + \quad S \quad \rightleftharpoons \quad S \cdot H_2O \qquad (5)$$

$$H_2O \quad + \quad A^- \rightleftharpoons (A \cdot H_2O)^- \qquad (6)$$

solution, where S and A⁻ represent a solvent and a basic anion, respectively. In the reaction (2), (3) and (4) the equilibrium may be attained rapidly, but ample time must be required for the equilibrium in the reaction (5) and (6) because of non-fluidity of the gel layer. From the reaction (2) and the equation (1), it can be seen that the lack of water in the gel layer according to the reaction (5) and (6) causes the decrease of the a_H^+, and consequently the potential of the electrode increases and the unfavorable response of the glass electrode in nonaqueous solution due to the slowness of the reaction (5) and (6). By means of dipping the glass electrode in the same solvent before measurement, the equilibrium in the reaction (5) can be attained to some extent, but this equilibrium is attained incompletly and the potential alters with time always even slightly.

The reaction (6) is dehydration from the gel layer. From the results that the potential fluctuates markedly in basic solution, it can be considered that the water in the gel layer acts as acid against to the A⁻ ion, which is partially adsorbed on the surface of the gel layer. This idea was supported by the experimental results that the potential of the electrode fluctuated with the basicity of solution. *Fig.* 7, in which the potential were plotted *vs.* log [Ox⁼]/[HOx⁻], is a schematic illustration: After the glass electrode kept in DMF had been dipped in the oxalate-bioxalte buffer solution of DMF (pH=17. 8) for four hours, the potential was measured. Then a little amount of picric acid was added to this solution in order to increase the concentration of bioxalate, and the potential was measured after standing for 30 min.. This procedure was carried out subsequently. In *Fig.* 7, the potential decreased in spite of increasing the concentration of the acid after the half-neutralized point in the titration curve. These results seemed

to be ascrtibed to the adsorption of the oxalate ion on the surface of the gel layer forming hydrate, which causes the decrease of the activity of water in gel layer and the equilibrium in reaction (2) is shifted left. As the acid is added the adsorbed oxalate ion is desorbed from the surface and a part of the combinated water is free. The theoretical line in *Fig.* 7 is the calibration curve of the glass electrode, prepared from the buffer solution of picric, salicylic and benzoic acid and their respective TEA-salt just after the measurement described above. If there was not any adsorption on the surface of the glass electrode, the potential plotted *vs.* log Cs/Ca would be laid on the line

The increase of the potential from that of theoretical value in the initial part of the potentiometric titration is approximately 50 mV, which is corresponding the decrease of the a_H^+ about 85% if not any other interaction.
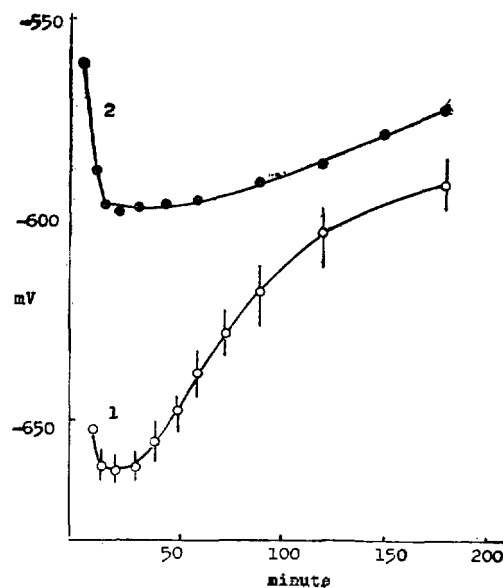

Fig. 7 Potentiometric titration cvrve of TEA-oxalate with picric in DMF. The theoretical line is the calibration curve prepared from the buffer solution of picric, salicylic and benzoic acid and their respective TEA-salt just after the potentiometric titration.

Table 1. Potentials in 1 mM DMF soluton of picric acid measured with the glass electrode which had been dipped in various pH of buffer solutions in DMF for 5 hours.

Buffer	pH	Potential
Picrate	3.0	253.4 mV
Salicylate	8.2	254.0
Acetate	14.3	284.1
Adipitate	15.9	289.5
Glutarate	16.9	300.6
Oxalate	17.2	324.4

In acidic solution, a stable potential was attained more rapidly than in basic solution. However, the potential measured in the same buffer solution varied with history of the glass electrode which had been used in various pH of buffer solution: when the potential in 0.001 M DMF solution of picric acid was measured with the glass electrode which had been dipped in various buffer solutions in Table 1 for 5 hours, it increased with the basicity of the buffer solution. Table 1 shows the results measured in DMF. In every case the slope of E vs. pH, cheked wity the buffer solution of salicylate and benzoate, was-59 ± 1 mV, but the more basic the buffer solution in which the glass electrode had been dipped, the more unfavorable was the time response. The reason is thought to be that the gel layer is dehydrated by anion during dip in basic buffer solution and the hydrating ability of anion is proportional to its basicity. The favorable response of the electrode could not be restored unless dipping it in water again. These behaviors as shown in Fig. 7 and in Table 1 were seen in methanol and AN too even to not a so much extent as in DMF.

In conclusion, the unfavorable time response of the glasselectrode in nonaqueous solution is due to the dehydration in gel layer, and the fluctuation of the potentia lis proportional to the basicity of solvent and solution. Therefore, in order to determine the pH value in nonaqueous solution with the glass electrode, the calibration of the electrode must be carried out before and after each measurement, and that for the determina tion of pH in a basic solution of DMF, it is preferred for reproduciblity that the potential is measured within 15~30 min. with the glass electrode stored in water. The experimental results are shown in Fig. 6.

Acknowledgement

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