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Use of pH–Sensitive ISFETs as Sensors for pH in Nonaqueous Solutions and for Proton Solvation

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Ta_2O_5– and Si_3N_4–type pH–sensitive ISFETs were found to respond almost in Nernstian ways to the pH in nonaqueous solutions and to the transfer activity coefficients of proton between different solvents. They responded much faster than the conventional glass electrode. This is of practical importance, because the response of the glass electrodes is unpractically slow in some nonaqueous solutions.

For pH measurements in nonaqueous solutions, pH–sensitive glass electrodes are usually used. Their response to pH ($=-\log a(H^+)$) has been confirmed to be Nernstian in various nonaqueous solvents.1) In nonaqueous solvents, however, the potential response of the glass electrodes is often very slow. In some cases it takes over an hour before an equilibrium potential is reached. Efforts have been made to improve the response time of glass electrodes but without sufficient success.2) In the present study, we used Ta_2O_5– and Si_3N_4–type pH–sensitive ISFETs in nonaqueous solutions and found that they can respond in nearly Nernstian ways to the pH in nonaqueous solutions. Their response was much faster than that of the glass electrode. They also responded in nearly Nernstian ways to the transfer activity coefficients of proton between different solvents. Many investigations have been reported on ISFETs, but, to the authors' knowledge, this seems to be the first use of ISFETs in nonaqueous solutions.3) The rapid response of the ISFETs is of practical importance in acid–base titrations and pH measurements in nonaqueous solvents as well as in the study of proton solvations in different solvents.

The Ta_2O_5– and Si_3N_4–type ISFETs were obtained from the Shindengen Industry Co. Ltd. In some solvents, it was necessary to protect the contact between the ISFET tip and the lead wire from the attack by the solvent. A Shindengen ISFET pH/mV meter was used to measure the gate voltage to 0.1 mV. The response of the ISFETs was compared with that of a conventional glass electrode (Horiba 1826A–06T). The potential of the glass electrode was measured with a conventional pH/mV meter. Propylene carbonate(PC) and γ–butyrolactone(γ–BL) were the pure products (F–PC and F–GBL) offered from Mitsubishi Petrochemical Co. Ltd. and were used without further purification. Other solvents were reagent grade Wako products and were used after purification by the methods recommended in Ref. 4). Trifluorometanesulfonic acid was a reagent grade Wako product and was used as received. Picric acid (HPic) was used after carefully drying the commercial product. Other electrolytes were the same as those used in the previous report.5) The experiments were carried out at room temperature between 20 and 25 °C.

Response to the pH in Nonaqueous Solutions: The response of the pH electrodes to the pH in nonaqueous solvents(S) was studied using the cell: Ag/5 mM $AgClO_4$, 25 mM Et_4NClO_4(S)//100 mM Et_4NClO_4(S)//C_a HPic+C_s Et_4NPic(S)/pH electrode, where the pH electrode was the Ta_2O_5– or Si_3N_4–type ISFET or the glass electrode. Some of the potential–time relations obtained by varying the C_a/C_s ratio are shown in Fig. 1. In obtaining Fig. 1, the Ta_2O_5–type ISFET and the glass electrode were inserted in the cell and the potentials of the two were recorded simultaneously against the common Ag/Ag^+ reference electrode. The response of the Ta_2O_5–type ISFET was always much faster than that of the glass electrode. The potential–log(C_a/C_s) relations at the Ta_2O_5–type ISFET are shown in Fig. 2. Though the slopes of the linear rela–tions were somewhat smaller than the Nernstian one, they were approximately the same as the slope which the ISFET showed for the pH in aqueous solutions (ca. 55 mV). The Si_3N_4–type ISFET also behaved in a similar manner. We may conclude that the ISFETs in nonaqueous solvents can respond almost in the same way as in aqueous solutions and have the advantage that they can respond much faster than the glass electrode.

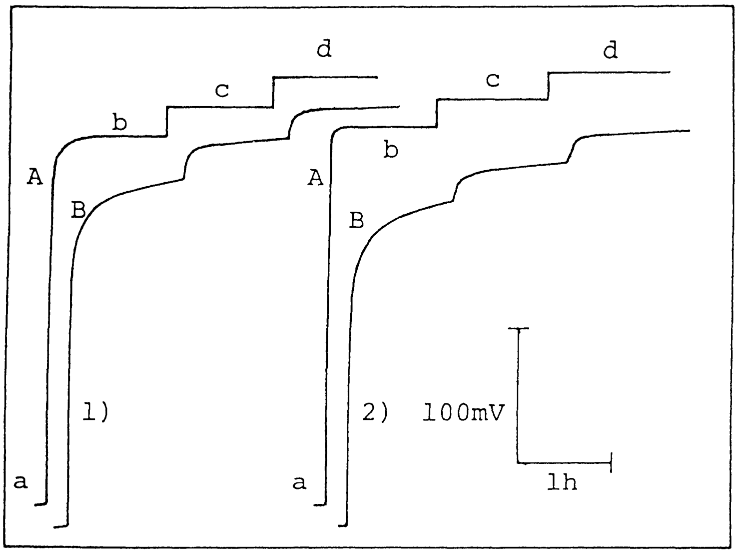

Fig. 1. Potential–time relations at the Ta_2O_5–ISFET and the glass electrode.
Curves 1A and 1B are in γ–BL and 2A and 2B in DMSO. Curves 1A and 2A are at the Ta_2O_5–ISFET and 1B and 2B at the glass electrode. Step a 5 mM Et_4NPic, b a+0.025 mM HPic, c a+0.05 mM HPic, d a+0.1 mM HPic.

Response to the Proton Solvation: The response to the proton solvation energy was studied measuring the emf of the cell, Ag/5 mM $AgClO_4$, 25 mM Et_4NClO_4(AN)//100 mM Et_4NPic(AN)//10 mM CF_3SO_3H(S)/pH electrode, for various solvents(S). The liquid junction potential between AN(acetonitrile) and S was assumed to be constant. In Fig. 3 are shown the relations between the emfs (in mV) and $\log\gamma_t(H^+,W\rightarrow S)$, where $\gamma_t(H^+,W\rightarrow S)$ is the transfer activity coefficient of H^+ from water to solvent S. We referred to Ref. 6) for the values of $\log\gamma_t(H^+,W\rightarrow S)$, though for PC we used the value previously obtained in our laboratory.[5)] The relations can be expressed by the equation $E = 55.8\log\gamma_t + 44$ (correlation coefficient R=0.9929) for the Ta_2O_5–type ISFET, $E = 52.6\log\gamma_t + 4$ (R=0.9929) for the Si_3N_4–type ISFET, and $E = 57.9\log\gamma_t + 46$ (R=0.9964) for the glass electrode. The slopes for the two ISFETs were somewhat smaller than the Nernstian slope but, here again, they were nearly equal to the slopes of the respective ISFETs in aqueous solutions. It is apparent that the two ISFETs as well as the glass electrode can be used as sensors

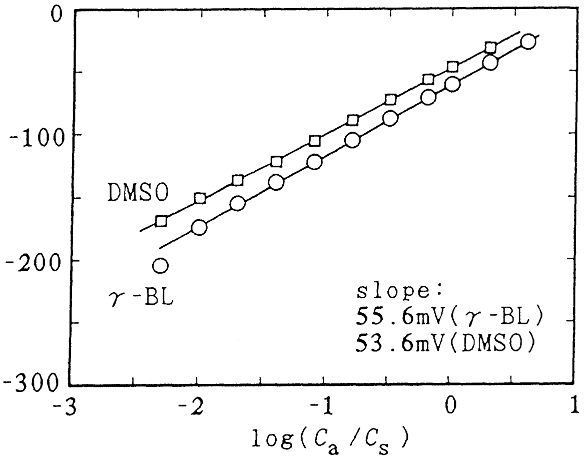

Fig. 2. Potential-log(C_a/C_s) relations in Et_4NPic–HPic solutions at the Ta_2O_5–ISFET (C_s = 5 mM).

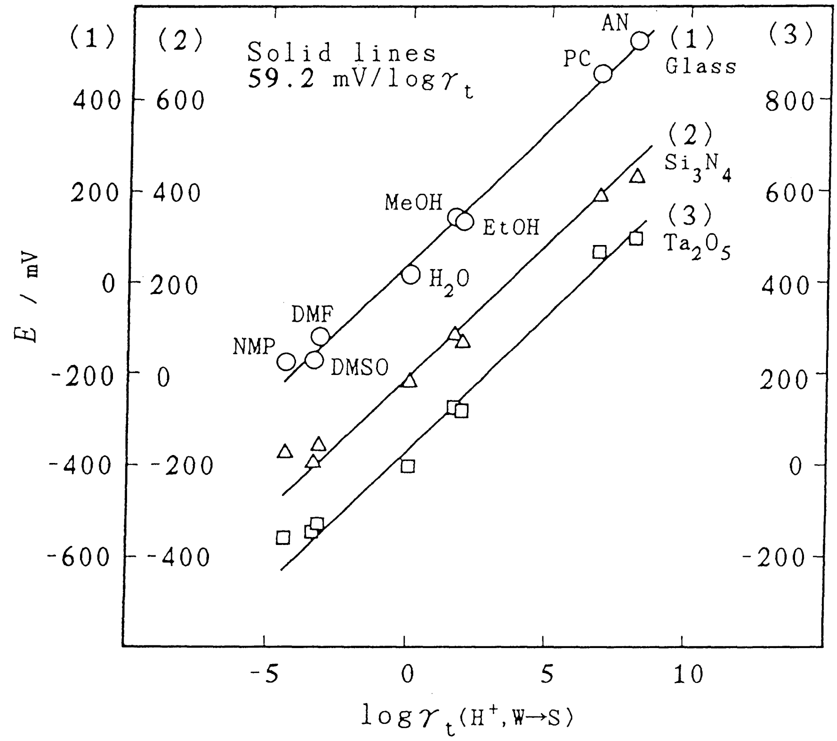

Fig. 3. Response of the Ta_2O_5– and Si_3N_4–type ISFETs and the glass electrode to $\log\gamma_t(H^+,W\rightarrow S)$.

for proton solvation. As to the response rate, the ISFETs were superior to the glass electrode. We have applied them to determine the values of $\log\gamma_t(H^+,W\rightarrow S)$ for solvents in which the values are not available yet. The results will be reported elsewhere.

As mentioned above, the Ta_2O_5– and Si_3N_4–type ISFETs were proved to be useful sensors for proton activities in nonaqueous solvents. For the response of the glass electrode in aqueous solutions, the hygroscopic layer on the glass surface plays an important role.[7)] In nonaqueous solutions, however, the layer seems to retard the establishment of the surface equilibrium. With the ISFETs without such a layer, the retardation does not occur. This may be the reason for the difference in the response rate between the glass electrode and the ISFETs. Works are now in progress in this laboratory to develop ISFETs which are more durable in nonaqueous solvents and to apply them to rapid nonaqueous titrations which have been difficult with a conventional glass electrode. The use of the ISFETs are also in progress in the study of acid–base equilibria in γ-butyrolactone which tends to react slowly with acids and bases.

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