ELECTROCHEMICAL PROPERTIES OF NA$^+$- AND K$^+$-SELECTIVE GLASS MICROELECTRODES

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ABSTRACT Electrochemical properties of Na$^+$-selective glass microelectrodes were studied and compared with those of K$^+$-selective glass microelectrodes. The selectivity of Na$^+$-selective glass microelectrodes depended on the ion concentration of test solutions. With aging, resistance of Na$^+$-selective microelectrodes increased and their selectivity for Na over K decreased. Na$^+$-selective microelectrode potential measured in NaCl solution remained constant with aging, while the potential measured in KCl solution decreased and became more positive. The changes in resistance and potential of Na$^+$-selective microelectrodes may be due to the effects of the less mobile cation, i.e., H$^+$ or K$^+$ on the Na ion exchange in the Na-sensing region. The results indicate that Na$^+$-selective microelectrodes must be used as soon after filling as possible. The selectivity of Na$^+$-selective microelectrodes increased with increase of the sensitive exposed-tip length, whereas their response time became slow due to a large recessed volume, indicating requirement of an optimum exposed-tip length for intracellular applications. The changes in the properties of Na$^+$-selective glass microelectrodes with aging contrasted with those of K$^+$-selective glass microelectrodes in which resistance decreased and K$^+$-selectivity increased. The K$^+$-selective microelectrodes required aging before use for a high selectivity and low resistance. The K$^+$-selective microelectrodes with low resistance after sufficient aging can be used without insulation to measure K$^+$ and Na$^+$ activities in aqueous solutions. The different properties between Na$^+$- and K$^+$-selective microelectrodes are understandable, because hydration of Na$^+$-selective glass is much less extensive than that of K$^+$-selective glass.

INTRODUCTION

Cation-selective glass microelectrodes are valuable tools for the measurement of cation activities in living cells and biological fluids. However, the application of this technique is complicated by the structure and small size of the microelectrode tip, and by the effect of glass hydration. This study is concerned with the electrochemical properties of the microelectrodes made from Na_2O—Al_2O_3—SiO_2 (NAS) 11-18 glass (Na$^+$-selective glass) and NAS 27-4 glass (K$^+$-selective glass). The properties investigated include cation-selectivity, resistance, Nernst slope, response time, and electrochemical potential across the glass membrane, which are important parameters for the electrode application. The glass electrodes must be soaked in an aqueous solution for practical uses. To evaluate the hydration effect the properties of Na$^+$-selective microelectrodes were compared with those of K$^+$-selective glass microelectrodes during aging of the electrodes. The present study shows that the changes in the properties of the microelectrodes made from NAS 11-18 glass are quite different from those of the microelectrodes made from NAS 27-4 glass.

The present study is also concerned with the use of uninsulated K$^+$-selective glass microelectrodes to measure K- and Na-ion activities in bulk solutions. This application takes

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advantage of the extensive hydration of glass at the tip of the microelectrodes. For intracellular application, the Na^+-selective microelectrodes were constructed with recessed tips as described by Thomas (1970, 1976) and some properties of such microelectrodes are presented. The results show that his design appears optimal for intracellular application, particularly for relatively small cells, even though the response time of the microelectrodes is relatively slow.

METHODS

Preparation of Cation-Selective Glass Microelectrodes

K^+-selective glass microelectrodes were made from Eisenman's NAS 27-4 glass (K^+-selective glass, Corning Glass Works, Medfield, Mass.). Micropipettes were drawn from the glass tubing by a vertical micropipette puller (David Kopf Instruments, Tujunga, Calif., model 700C). The glass tubing had an inner diameter of 0.020 ± 0.003 in and outer diameter of 0.040 ± 0.004 in. The drawn micropipettes had a tip diameter <1 μm. The tip of the micropipettes was sealed by heating so that a glass membrane could be formed (for details, see Lee and Fozzard, 1974). The microelectrodes were filled first with methanol by evacuation; methanol was then replaced by distilled water, and finally by a 3-M KCl solution. Some of the microelectrodes were filled by injecting the 3-M KCl solution directly with a syringe.

Na^+-selective microelectrodes were made from Eisenman's NAS 11-18 glass (Na^+-selective glass, Microelectrodes, Inc., Londonderry, N.H.). Micropipettes were drawn from the glass tubing by a vertical micropipette puller (Narashige Scientific Instrument Laboratory, Tokyo, Japan, model PE-2), since Na^+-selective glass is much harder than K^+-selective glass. The glass tubing had a similar diameter to that of K^+-selective glass tubing. The drawn micropipettes had a tip diameter <1 μm. The tip of the micropipettes was sealed by heating; sealing of Na^+-selective glass micropipettes required much higher heat. Thomas' design (1976) was used for construction of the Na^+-selective microelectrodes. A sealed Na-micropipette was dropped into an insulating glass micropipette. The insulating micropipettes with a tip diameter <1 μm were made from a borosilicate glass (Corning Glass Works, Code 7740). The insulating micropipette with a Na^+-selective micropipette in the inside was carefully positioned so that the shank could be near a heating wire loop. Then, heat was applied to melt the insulating glass. After the insulating glass micropipette was fused with the Na^+-selective micropipette and was cooled, the stem of the Na^+-selective micropipette was removed by breaking the shank of the Na^+-selective micropipette, broken by gentle tapping of the insulating micropipette. The microelectrodes were filled with 3 M NaCl solution by a syringe. Remaining air bubbles were removed by thin and long glass micropipettes and gentle heating. Some of the microelectrodes were made using Hinke's design (1959).

Measurement of Microelectrode Potentials and Resistance

Potential and resistance of K^+-selective glass microelectrodes were measured by the methods described previously (Lee and Fozzard, 1974) whereby the potential difference across the glass membrane of the microelectrodes can be measured. The electrochemical cell for measurement of Na^+-selective microelectrode potentials was similar to that for K^+-selective microelectrode potentials, except for the use of Ag/AgCl electrode in the Na^+-selective microelectrode side. With this system, the resistance and the selectivity of the Na^+-selective microelectrodes can be obtained as described previously (Lee and Fozzard, 1974). In the measurement of the glass membrane potential (E_M) of Na^+-selective microelectrodes, however, the potential difference between Hg/Hg_2Cl_2 and Ag/AgCl electrodes should be taken into account, since they are not equal. To obtain E_M, the potential difference between Hg/Hg_2Cl_2 and Ag/AgCl electrodes was subtracted from the total potential. The potential difference can be measured as the potential between the saturated KCl agar bridge and the Ag/AgCl electrode in 3 M NaCl solution. Microelectrode potentials and resistances were measured with a tip length of 2 mm immersed into test solutions, unless a specific length of the immersed portion of the tip was indicated.

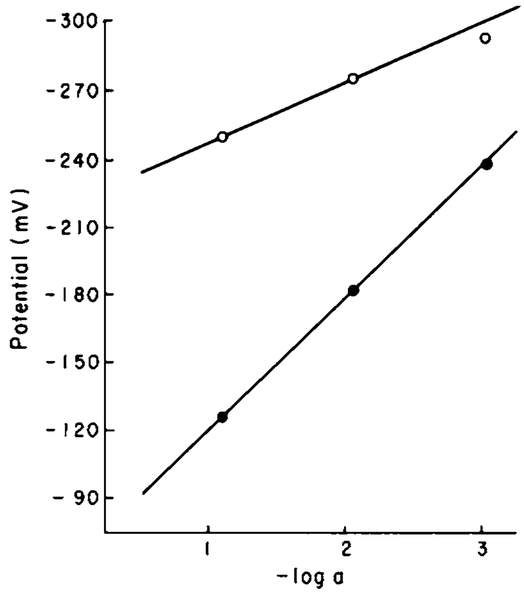

FIGURE 1 The relation between Na^+-selective glass microelectrode potentials and activities of Na and K ions. The potentials were measured in 1, 10, and 100 mM NaCl (●) and KCl (○) solutions. *a* is the activity of Na or K ion.

RESULTS

Selectivity and Resistance of Cation-Selective Glass Microelectrodes

In Fig. 1, potentials of a typical Na^+-selective glass microelectrode were plotted against Na^+ and K^+ activities. The potentials in NaCl solutions were measured about 3 h after the microelectrode was aged in 3 M NaCl solution. The relation between the microelectrode potential and Na-ion activity is linear with a slope of 59.6 mV, which is close to the ideal slope of 59.1 mV (2.303 RT/F = 59.1 mV at 25°C). The relation between the microelectrode potential and K-ion activity is not linear and the slope was lower than that in NaCl solution. The difference[1] between the potentials measured in NaCl and KCl solutions with the same concentration decreased as the concentration decreased. This result indicates that selectivity of the microelectrode for Na^+ over K^+ depends on the concentration of the test solutions; the selectivity decreases with decreasing concentration.

The selectivity coefficient and resistance of Na^+-selective microelectrodes were measured during storage (aging) in 3 M NaCl solution. Fig. 2 illustrates the changes in selectivity coefficient and resistance of a typical Na^+-selective microelectrode with aging. 16 microelectrodes were studied and the results were similar to that shown in Fig. 2. The selectivity coefficient of the microelectrode increased with aging (the selectivity for Na^+ over K^+ decreased with aging). On the other hand, the resistance of the microelectrode increased in

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[1] The potential difference may be used to determine the selectivity of cation-selective microelectrodes (Lev, 1969). The selectivity coefficient (k_{NaK}) of a Na^+-selective microelectrode can be represented by the equation, $k_{NaK} = \exp(E_K - E_{Na}) F/RT$ where $(E_K - E_{Na})$ is the potential difference. A decrease in selectivity coefficient means an increase in selectivity.

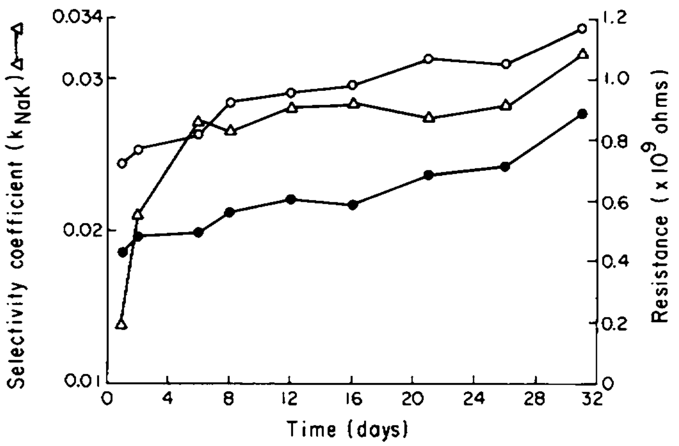

FIGURE 2 The changes in resistance and selectivity coefficients of a Na^+-selective glass microelectrode. The selectivity coefficients (Δ) were determined in 100 mM NaCl and KCl solutions. The filled (●) and open (○) circles represent the microelectrode resistances in 10 mM NaCl and KCl solutions, respectively.

both NaCl and KCl solutions. The resistance of the microelectrode is greater in KCl solution than that in NaCl solution.

Fig. 3 shows the changes in the selectivity coefficient and resistance of Na^+-selective microelectrode for a period of approximately 40 h after filling. The initial selectivity coefficient (approximately 15 min after filling) was 0.0044. This value is similar to that (0.005) observed by Hinke (1959 and 1961). Then the selectivity coefficient increased to a value of 0.023 approximately 42 h after aging (i.e., the Na^+/K^+ selectivity decreased). Five microelectrodes tested gave results similar to those shown in Fig. 3. Their initial selectivity coefficients were between 0.004 and 0.008, and approximately 40 h after aging they were between 0.02 and 0.03. Fig. 3 also shows an increase in the microelectrode resistance with aging for that period. The results indicate that Na^+-selective microelectrodes should be used as soon after filling as possible for intracellular application.

Selectivity coefficients of Na^+-selective microelectrodes were determined from the electrode potentials measured in NaCl and KCl solutions. Fig. 4 *A* shows the changes in the microelectrode potentials with aging. Eleven microelectrodes tested showed similar results. There were no substantial changes in the microelectrode potentials measured in 10, 100 mM, and 3 M NaCl solutions. Note that 3 M NaCl solution is identical with the filling solution. Thus, the Nernst slope of the microelectrode ($\Delta E/\Delta \log a_{Na}$) remained constant with aging. The microelectrode potential in 3 M NaCl, known as the asymmetry potential, also remained constant. However, the microelectrode potential measured in 100 mM KCl solution decreased with aging. The change in selectivity coefficient (Figs. 2 and 3) may be ascribed to the potential change in KCl solution. Fig. 4 *B* shows the potential changes of a representative K^+-selective glass microelectrode with aging in 3 M KCl solution. The potentials were measured in 10 mM, 100 mM, 3 M KCl solutions, and 100 mM NaCl solution. The microelectrode resistance fell markedly with aging, which is consistent with our previous results (Lee and Fozzard, 1974). About 2 d after aging, the microelectrode potentials in 100 and 10 mM KCl solutions were −62 and −108 mV, respectively. The microelectrode potentials increased with aging and reached a relatively constant value of −80 and −135 mV

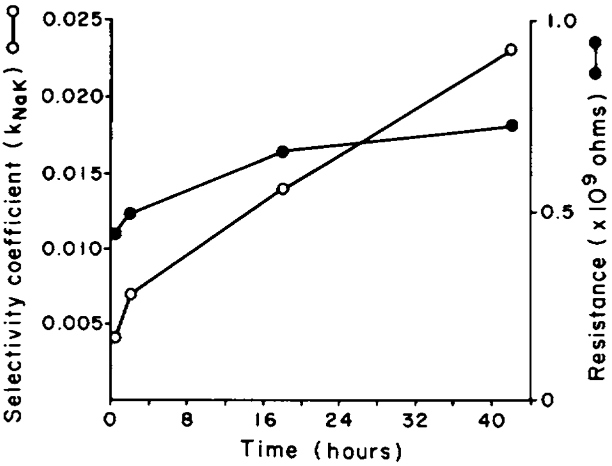

FIGURE 3 Changes in selectivity coefficient and resistance of a Na^+-selective glass microelectrode during 40 h aging.

in the fifth week after aging. It is interesting to note that −80 and −135 mV are the equilibrium potentials of the microelectrode glass membrane. The equilibrium potentials were calculated from the mean ionic activities of KCl of the inner solution (3 M) and outer solutions (100 and 10 mM) of the microelectrode. $E = 2.303\ RT/F \log (0.1 \times 0.7701/3.0 \times 0.572) = -79.8$ mV. $E = 2.303\ RT/F \log (0.01 \times 0.902/3.0 \times 0.572) = -134.7$ mV. Thus, it appeared that the microelectrode potentials changed from a nonequilibrium value to an equilibrium value with aging. These results suggest that the glass membrane became ideally permeable to K^+ as the glass membrane resistance decreased. In Fig. 4 *B*, it can be seen that with aging the potential change in 10 mM KCl solution (135 mV − 108 mV = 27 mV) is greater than that in 100 mM KCl solution (80 mV − 62 mV = 18 mV). This result indicates that with aging the rate of potential change in 10 mM KCl is greater than that in 100 mM KCl. Because of the difference in the rate of the potential changes between 10 and 100 mM KCl, the Nernst slope of the microelectrode increased with aging. In the microelectrode used in Fig. 4 *B*, the slope ($\Delta E/\Delta \log a_K$) increased from 50 to 59 mV. Fig. 4 *B* also shows the change of the microelectrode potential in 100 mM NaCl solution. The selectivity coefficient of the microelectrode can be determined from the difference between the potentials measured in 100 mM KCl and NaCl solutions (Lee and Fozzard, 1974). The potential difference increased with aging. This indicates that the selectivity of the microelectrode for K^+ over Na^+ increased with aging. Fig. 4 *B* also shows the change in the microelectrode potential measured in 3 M KCl (asymmetry potential). With aging, the potential changed and approached zero. The possible causes of the asymmetry potential have been discussed by Bates (1965), who suggested that the potential may arise from an asymmetry between the inside and outside of the glass membrane.

Selectivity, Resistance, and Exposed-Tip Length of Na^+-Selective Microelectrodes

One of the most important features in electrode construction is the provision of adequate electrical insulation to eliminate leakage paths between the two sides of the responsive

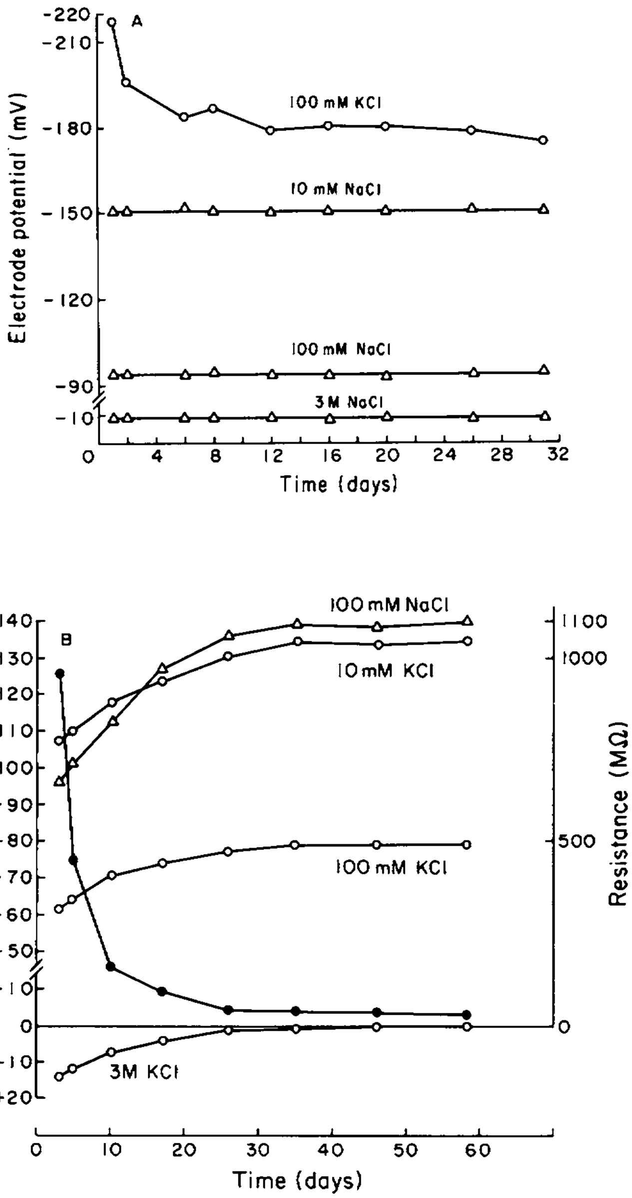

FIGURE 4 (*A*) Relation between Na$^+$-selective glass microelectrode potential and aging time. The open triangles represent the potentials measured in 10 and 100 mM, and 3 M NaCl solutions. The open circles represent the potentials measured in 100 mM KCl. (*B*) The changes in K$^+$-selective glass microelectrode potential with aging. The open circles represent the potentials measured in 10, 100 mM, and 3 M KCl solutions. The open triangles represent the potentials measured in 100 mM NaCl solution. The filled circles represent the change in resistance of the microelectrode in 100 mM KCl solution.

membrane (Mattock, 1965). Insulation may be one of the most difficult steps in the construction of glass electrodes. The insulation is particularly important in Na^+-selective microelectrodes in which a small responsive membrane is exposed and a high resistance is predicted and observed.

Generally, there are two different designs for insulation of Na^+-selective glass microelectrodes. One is Hinke's design in which, except for a certain length from the tip, the microelectrode is insulated with a high resistance material such as a nonconducting glass (Hinke, 1961). The microelectrode tip is protruded outside the tip of the insulating glass pipette and the response glass is directly in contact with a test solution. The other is Thomas' design in which the tip of the microelectrode is in the inside of the outer insulating glass pipette (Thomas, 1976), the so-called "recessed-tip microelectrode." In this design, the response glass is in contact with a test solution through a small open tip of the insulating micropipette. The recessed-tip microelectrode was designed particularly for application in relatively small cells.

Both types of the Na^+-selective glass microelectrodes were made and some of their properties were studied. Fig. 5 illustrates some properties of representative microelectrodes of both types. Fig. 5 *A* shows the potentials measured with the microelectrode of Hinke's design in NaCl and KCl solutions of 10 and 100 mM. These potentials were measured about 3 h after the microelectrode was filled. The resistance values ($<10^9\ \Omega$) were relatively low since the exposed-tip length of 1.8 mm was long. The selectivity coefficient of the microelectrode was

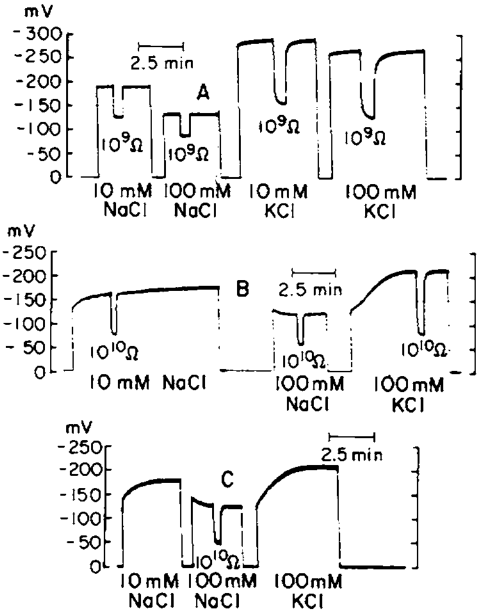

FIGURE 5 Potential recordings with Na^+-selective glass microelectrodes insulated with usual glass (Corning 7740). (*A*) The Na^+-selective microelectrode tip was protruded from the tip of insulating micropipette. $k_{NaK} = 0.0074$; $L = 1.8$ mm. (*B*) and (*C*) The Na^+-selective microelectrode tip was recessed in the tip of insulating micropipette. L represents the exposed length of Na^+-sensitive tip. In each recording, the potential drop was obtained to determine the microelectrode resistance. (*B*) $k_{NaK} = 0.023$; $L = 90\ \mu m$. (*C*) $k_{NaK} = 0.031$; $L = 46\ \mu m$.

0.0074 as determined from the potentials measured in 100 mM NaCl and KCl solutions. In other words, the microelectrode is 135 times more selective to Na^+ than K^+. It can be seen that the response time of the microelectrode is faster in NaCl solutions than in KCl solutions. The potential recordings also show that the slope is greater in NaCl solution than in KCl solution. Fig. 5 *B* and *C* show the potentials measured with recessed-tip microelectrodes. Before the measurements, the tips of the microelectrodes were immersed in 100 mM NaCl solution for about 3 h to fill the recess space and age for a period similar to that in Fig. 5 *A*. The resistances of the microelectrode used in Fig. 5 *B* were 1.1×10^{10} and $1.7 \times 10^{10}\ \Omega$ in 100 mM NaCl and KCl solutions, respectively. The resistance of the microelectrode used in Fig. 5 *C* was $1.8 \times 10^{10}\ \Omega$ in 100 mM NaCl solution. These resistance values of the recessed-tip microelectrodes were much higher than those of the protruded-tip microelectrode since the exposed-tip lengths (90 and 46 μm) of the recessed-tip microelectrodes were shorter than that of the protruded microelectrode. The selectivity coefficients of the microelectrodes used in Fig. 5 *B* and *C* were 0.023 and 0.031, which were greater than that of the microelectrode used in Fig. 5 *A*. In other words, the microelectrodes with high resistance and short exposed-tip length had a lower selectivity for Na^+ over K^+ than those with low resistance and long exposed-tip length. The response time of the recessed-tip microelectrodes was slower than that of the protruded microelectrodes. The slow response time may be due to the recess space occupied by fluid, which must be equilibrated with the test solution through a small tip of the insulating micropipette. Nine recessed-tip microelectrodes with different exposed-tip length from 30 to 120 μm were made and their selectivity coefficients were determined from the potentials measured in 100 mM NaCl and KCl solutions. The selectivity coefficients were between 0.01 and 0.04. The selectivity coefficient decreased as the exposed-tip length increased. Thus, the microelectrodes with a long exposed-tip length have a greater selectivity for Na^+ over K^+ than those of a short exposed-tip length. However, the microelectrodes with a long exposed-tip length have a slow reponse time since they have a long recess space. The results suggest that the recessed-tip Na^+-selective microelectrodes require an optimum length of exposed tip for high selectivity, low resistance, and fast response time.

Application of Uninsulated K^+-Selective Microelectrodes

With aging, the resistance of K^+-selective glass microelectrodes fell markedly and their selectivity increased (Lee and Fozzard, 1974 and Fig. 4 *B*). The decrease in resistance was interpreted to indicate that the thin glass membrane at the microelectrode tip was completely hydrated and the resistance of the glass membrane at the tip was much lower than that of the glass membrane of the microelectrode stem. This suggests that after sufficient aging the K^+-selective microelectrodes can be used without insulation. The hydrated glass membrane with low resistance at the tip and the nonhydrated glass membrane with high resistance along the microelectrode stem may be analogous to the responsive membrane and the electrode insulation, respectively. The sufficiently aged K^+-selective glass microelectrodes were tested to see if they could be used to measure ionic activities in aqueous solutions without insulation. As seen in Fig. 4 *B*, the resistance of the 2-d-aged microelectrode was about $10^9\ \Omega$ with an immersed-tip length of 2 mm. The resistance of the 40-d-aged microelectrode was $2 \times 10^7\ \Omega$ with an immersed-tip length of 2 mm. Thus, the resistance of the more aged microelectrode was much lower than that of the less aged microelectrode. In the high resistance microelectrode, the potentials were dependent on the immersed-tip length in a test solution. The possible reasons for the potential changes have been described previously (Lee and Fozzard, 1974). When the electrode potentials vary in a test solution, being dependent on the immersed-tip length, the ionic activity cannot be determined. Therefore, the electrode must be insulated with a high resistance material and a constant area may be exposed. With the low resistance microelectrode, the potentials did not depend on the tip length immersed into a given test solution. The potential differences observed between the immersed-tip lengths of 2 and 4 mm were within 1 mV when the microelectrode resistance was less than 100 MΩ.

K- and Na-ion activities were measured with a low resistance (about 30 MΩ) microelectrode without insulation. The experimentally determined activity coefficients of K and Na ions were compared with the calculated activity coefficients of K and Na ions. The results are shown in Fig. 6. This is a method similar to that described by Bates and Alfenaar (1969). The activity coefficients were calculated by means of the extended Debye-Hückel equation (Butler, 1964). The experimental values of K^+ and Na^+ activity coefficients were determined in 1, 5, 10, 100, and 200 mM KCl and NaCl solutions. The experimental values of the activity coefficients agree with the calculated activity coefficients. The departures of the experimental values from the curve are within 1 mV. The discrepancy for Na ions is greater than that for K ions, and may be due to residual liquid junction potentials, and/or the possibility that the departure may be caused by the inadequacy of the extended Debye-Hückel equation. Nevertheless the agreement is quite satisfactory, so that the microelectrodes can be used to measure the accurate activities of K and Na ions in the solutions.

DISCUSSION

Since Na^+- and K^+-selective glass electrodes were introduced by Eisenman (1957, 1962), cation-selective electrodes have been applied for measurements of Na^+ and K^+ activities in biological systems. For extracellular application, cation-selective glass electrodes have been used to measure Na^+ and K^+ activities in biological fluids (Friedman, 1967; Moore, 1967). For intracellular application, various types of the cation-selective microelectrodes have been

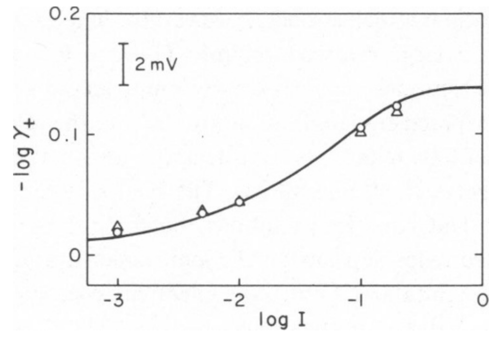

FIGURE 6 Experimental values (open circles and triangles) of $-\log \gamma$ are compared with the values (curve) calculated from the extended Debye-Hükel equation at different ionic strength (I). ○ − γ_K; △ − γ_{Na}.

developed, and Na^+ and K^+ activities were measured (for comprehensive reviews, see Lev and Armstrong, 1975; Walker and Brown, 1977).

The resistances of Na^+-selective microelectrodes with an exposed-tip length of about 2 mm were in the range of 0.3×10^9 to 0.7×10^9 Ω in 100 mM NaCl and KCl solutions. The resistance of the microelectrodes increased with aging. The increase in the resistance of Na^+-selective microelectrodes is quite different from the observation in macroscopic Na^+-selective glass electrodes in which the resistance did not increase with aging. Eisenman[2] suggested that the resistance increase may represent the effect of exchange of the most mobile Na^+ by the less mobile H^+ or K^+, and the effect of the mixed-alkali ion (Eisenman et al., 1967). The change in resistance contrasts with the change in resistance of K^+-selective glass microelectrodes. The resistance of K^+-selective microelectrodes decreased with aging (Lee and Fozzard, 1974). These observations are understandable because hydration on Na^+-selective glass is much less extensive than that of K^+-selective glass (Eisenman, 1965, 1969). In this study, Na^+-selective microelectrodes with the exposed-tip length of 100 to 20 μm had the resistance of 10^{10} to 10^{11} Ω. These resistance values agree with those reported by other investigators. The resistances reported by Thomas (1976) were 10^{10}–10^{11}Ω for the microelectrodes with exposed-tip length of 200–20μm. The resistances observed by Hinke (1959) were also 10^{10}–10^{11} Ω for the microelectrodes with an exposed-tip length of about 150 μm and 1–4-μm wall thickness. The higher resistance of Na^+-selective microelectrodes in KCl than in NaCl solution (Fig. 3) agrees with the results reported by Thomas (1976). The higher resistance is also expected from the lower mobility of K^+ than Na^+ in both dry and hydrated glass (Eisenman, 1965, 1967, and 1969).

The selectivity of Na^+-selective microelectrodes for Na^+ over K^+ decreased with aging. This observation is quite in contrast with that from K^+-selective glass microelectrodes, in which the selectivity for K^+ over Na^+ increased with aging (Lee and Fozzard, 1974). This result indicates that Na^+-selective glass microelectrodes must be used as soon after filling as possible. The selectivity decrease of the Na^+-selective microelectrodes with aging also contrasts with the observation in the macroscopic Na^+-electrodes. The selectivity decrease may also be explained by the effects of the less-mobile ion, i.e., H^+ or K^+ together with the mixed-ion effect (Eisenman et al., 1967). The selectivity of Na^+-selective microelectrodes depended on the exposed-tip length. The selectivity increased as the exposed-tip length was increased. In the recessed-tip microelectrodes, however, the long exposed-tip length resulted in a slow reponse time and a large recessed volume. These results suggest that intracellular application of the microelectrodes requires an optimum length of the exposed tip. In the microelectrode with the exposed-tip length of 40 to 100 μm, the selectivity coefficient (k_{NaK}) was usually in the range of 0.04 to 0.01. For intracellular application, the optimum lengths of the exposed tip may be between 40 and 80 μm. The Na^+-selective microelectrodes must be carefully calibrated using NaCl and KCl solutions, including their mixture solution, since the selectivity of the microelectrodes depends on the ionic concentration. In the microelectrodes with a long exposed-tip length (about 2 mm), the selectivity coefficient was about 0.004 about 15 min after filling. This value is quite similar to that (0.005) observed by Hinke (1959, 1969). The relation between the selectivity and the exposed-tip length is understandable from

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[2] Eisenman, G. Personal communication.

that between the microelectrode resistance and the exposed-tip length, since the microelectrodes with high resistance had usually poor selectivities.

It was shown that K^+-selective glass microelectrodes without insulation can be used to measure K^+ and Na^+ activities in aqueous solutions. With proper arrangement of the reference electrode, they can be applied to measure the ion activities in a small quantity of test samples since the length of the low resistance position of the tip may be roughly 30 μm (Lee and Armstrong, 1974). The microelectrodes without insulation are restricted to extracellular applications. However, for intracellular use, where part of the hydrated glass extends through the cell membrane to the outside, insulation may still be necessary.

Some of the work on K^+-selective glass microelectrodes was done in the laboratory of Dr. Harry A. Fozzard. I appreciate the valuable assistance of Mr. Jeffrey Sokol in some electrical potential measurements and the generous gift of Na^+-selective glass tubings from Dr. K. S. Lee.

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