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RESPONSE TIME CURVES OF AMMONIUM ION-SELECTIVE ELECTRODE OF TUBULAR SHAPE

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In order to reproducibly measure response time curves of a poly (vinyl chloride) matrix membrane ammonium ion-selective electrode, an experimental setup composed of a tubular flow-through electrode was constructed. The data were analyzed by the curve fitting method using two theoretical equations, that based on the assumption of the film diffusion and that of the diffusion within the membrane.

In recent years a large number of neutral carrier based ion-selective electrodes have appeared. Usually the dynamic behavior of these electrodes is not satisfactorily characterized compared with the selectivity behavior. This trend is due to the difficulties in obtaining the reproducible data of response times under the step change of concentration. Response time curves (potential vs. time curves) are greatly dependent on the flowing conditions of the bathing solution and are subject to electrical noise. Lindner and co-workers$^{1,2)}$ studied the dynamic chracteristics of valinomycin based potassium ion-selective electrodes using their apparatus mounted with the solution jets perpendicular to the electrode surface. Akiyama et al.$^{3)}$ also examined the factors affecting the transient response properties of the valinomycin electrode, and concluded that the diffusion through a stagnant solution layer was rate controlling.

We report here an experimental method and the preliminary results of the response time studies of neutral carrier electrodes using the ammonium responsive poly (vinyl chloride) (PVC) membranes based on antibiotics actins$^{4)}$. In order to exactly control the thickness of the stagnant layer, we attempted to apply a tubular flow-through electrode configuration to the measuring cell system.

Macrotetrolide actin mixture (tetranactin 65%, trinactin 30%, dinactin 5%) was kindly supplied by Research Laboratories, Chugai Pharmaceutical Co.,Ltd. The electrode membrane consisted of ligand (5%), dibutyl sebacate (70%), and PVC (25%). The tubular flow-through electrode unit was prepared in the manner mainly after Fraticelli and Meyerhoff$^{5)}$. Tygon tubing of internal diameter 0.8 mm was used. The mixture containing membrane components was cast into a cut opening (ca. 2 mm diameter) of the side of the tubing, within which a syringe needle was inserted as a mandrel. Thus the membrane having a smooth cylindrical surface inside the tube was formed.

Figure 1 schematically illustrates an experimental set-up for the response

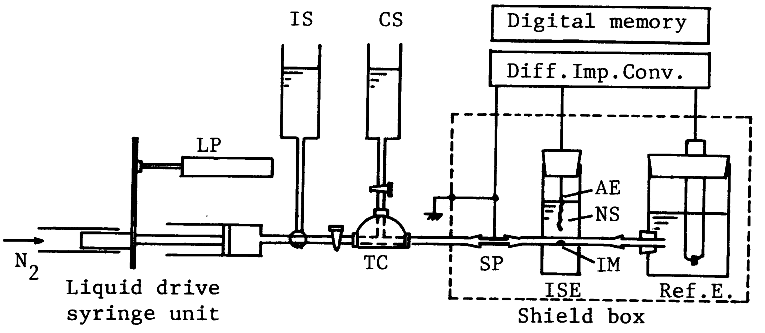

Fig. 1. Experimental set-up for the fast response time measurement. LP: Linear potentiometer, IS: Injection solution, CS: Conditioning solution, TC: Three way connecter, SP: Stainless pipe, AE: Ag/AgCl electrode, NS: NH_4Cl solution, IM: Ion sensitive membrane.

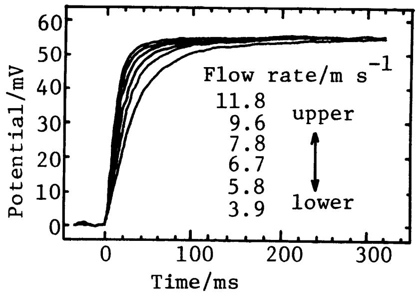

Fig. 2. Typical response time curves for 10^{-4} to 10^{-3} mol dm^{-3} NH_4Cl.

time measurement. A liquid drive syringe unit was constructed by modifying Union Giken Sample Mixing Device MX-7 and by attaching Gas Drive Unit-A. A linear potentiometer (LP in Fig. 1) was connected with the syringe unit to measure the flow rate of the bathing solution. To eliminate electrical noise, a stainless pipe (SP) was inserted between the three way connector (TC) and the tubular electrode (IM) and was connected to the ground terminal of a home made differential impedance converter. A silver wire coated with silver chloride (AE) was used as inner reference electrode. A conventional silver-silver chloride electrode was placed in the reference electrode compartment containing the waste solutions. Step changes in solution concentrations were attained by turning cocks and triggering the gas drive unit to inject new solution into the tubular electrode which had already been exposed to conditioning solution. In all measurements, 0.1 mol dm^{-3} lithium chloride was used as supporting electrolyte to eliminate streaming potential. All measurements were made at room temperature (ca. 20°C).

Figure 2 shows typical response time curves at various flow rates. Evidently these curves depend on the flow rate and are virtually unsusceptible to electrical noise.

We attempted curve fittings using two theoretical equations described by Morf et al.[6] An exponential type equation which is based on the assumption that the diffusion of fresh electrolyte into the static layer controls the response time is as follows:

$$E(t) = E(\infty) + s \log \{1-(1-\frac{a_i^o}{a_i})\, e^{-t/\tau'}\} \qquad (1)$$

with a time constant of $\tau'=\delta^2/(2D')$, where E(t) is the potential measured at the time t, $E(\infty)$ is the final potential after the activity step, s is the slope of the calibration graph, a_i^o is the activity of the conditioning solution, a_i is the activity of the newly injected solution, δ is the thickness of the aqueous adhering layer, and D' is the diffusion coefficient of ion within the adhering layer. Another is a square-root type one derived from the assumption that the diffusion within the membrane is regarded as rate controlling:

$$E(t) = E(\infty) + s \log \{1-(1-\frac{a_i^o}{a_i}) \frac{1}{\sqrt{t/\tau}+1}\} \qquad (2)$$

with a time constant of $\tau = DK^2\delta^2/(\pi D'^2)$, where D is the mean diffusion coefficient of electrolyte within the membrane and K is the salt distribution constant. These equations were transformed into linearized ones and were employed in the fittings using the method of least squares; the following equation was obtained from Eq. 1 and Eq. 2 respectively:

$$-\ln \frac{1-10^{(E(t)-E(\infty))/s}}{1-a_i^o/a_i} = \frac{1}{\tau'} t - \frac{\theta}{\tau'} \qquad (3)$$

$$\{\frac{1-a_i^o/a_i}{1-10^{(E(t)-E(\infty))/s}} - 1\}^2 = \frac{1}{\tau} t - \frac{\theta}{\tau} \qquad (4)$$

where θ is an adjustable parameter with respect to time additionally introduced for the following adjustment. Figure 3 illustrates an example of curve fitting procedure using the response time data for the concentration change from 1×10^{-4} mol dm^{-3} to 2×10^{-4} mol dm^{-3} ammonium chloride. The plot of the l.h.s. on Eq. 3 is best fitted in a range of time from 10 ms to 55 ms; the correlation coefficient is more than 0.999 and the standard error is 0.09 mV. After about 55 ms, a deviation notably occurs. On the other hand, the plot on Eq. 4 is considerably fitted in a range from 50 ms to 160 ms with the correlation coefficient of 0.996 and the standard error of 0.06 mV. For these data, each time constant estimated from the reciprocal slope of the fitted straight line is 29.3 ms and 0.87 ms for Eq. 3 and Eq. 4 respectively. Figure 4 shows how the theoretical curves obtained by the least squares determinations of the time constant and the adjustable parameter fit the experimental results, where the curves are extended beyond the ranges of time mentioned above.

In the same manner, the time constants of the exponential type equation (Eq. 1) and $t^{-\frac{1}{2}}$ type one (Eq. 2) for different concentration changes of ammonium

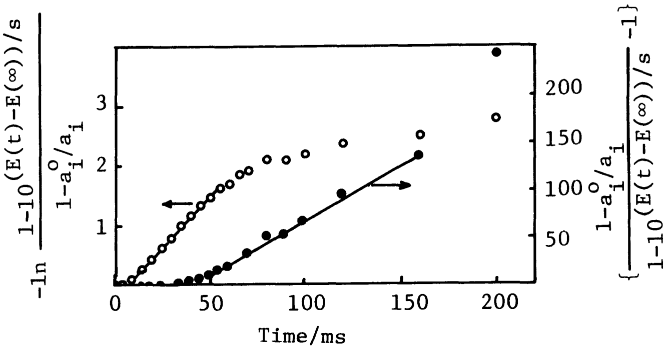

Fig. 3. Linear regression. Each term on the l.h.s. of Eq. 3 (○) and Eq. 4(●) is plotted against time t using the data for concn change from 1×10^{-4} to 2×10^{-4} mol dm^{-3} NH_4Cl with the flow rate of 3.7 m s^{-1}.

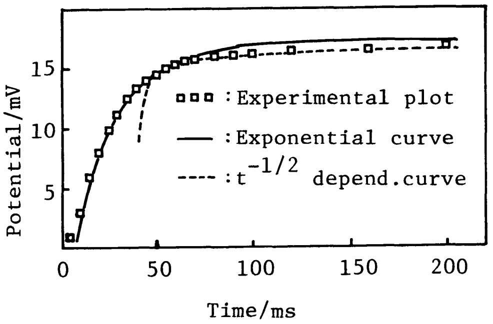

Fig. 4. Theoretical curves and the experimental data. Time constants and adjustable parameters were estimated by the procedure described in Fig. 3.

chloride solution were measured (Table 1). It is obvious that the time constants of the exponential type equation have almost the same values over the different concentration changes and that the measurements are highly reproducible from the results of standard deviations. On the other hand, the time constants of the $t^{-\frac{1}{2}}$ type equation have less reproducible values than those of the exponential type one as shown in Table 1.

Table 1. Time Constants of the Exponential Type Equation (Eq. 1) and the $t^{-\frac{1}{2}}$ Type One (Eq. 2) for Different Concentration Changes. Flow Rate: 3.7 - 3.8 m s^{-1}

NH_4Cl concn change	τ' in Eq. 1	std. dev.	τ in Eq. 2	std. dev.
mol dm^{-3}	ms	ms	ms	ms
$1\times10^{-4} \rightarrow 2\times10^{-4}$	27.7	1.3	0.81	0.29
$1\times10^{-4} \rightarrow 1\times10^{-3}$	27.5	1.0	0.76	0.05
$2\times10^{-4} \rightarrow 1\times10^{-4}$	26.6	0.6	0.56	0.11
$1\times10^{-3} \rightarrow 2\times10^{-3}$	26.3	1.1	0.65	0.15
$1\times10^{-3} \rightarrow 1\times10^{-2}$	27.5	0.8	0.64	0.02
$2\times10^{-3} \rightarrow 1\times10^{-3}$	24.4	1.6	0.50	0.24
$1\times10^{-2} \rightarrow 2\times10^{-2}$	27.4	0.6	0.92	0.18
$1\times10^{-2} \rightarrow 1\times10^{-1}$	33.1	1.0	1.11	0.03
$2\times10^{-2} \rightarrow 1\times10^{-2}$	26.6	1.4	0.38	0.13

An application of tubular flow-through electrode to the measurement of the response time curve yields reproducible data which could be analyzed by the curve fitting method using two theoretical models. The first part of the yielded response time data was fitted by the theoretical curve based on the film diffusion, while the next part was fitted by that based on the diffusion process within the membrane. To understand the observations in this study, further examinations on the curve fittings with various equations are now in progress. Moreover the measurements with different electrolytes are under way.

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