Response Time Curves of Neutral Carrier Membrane Electrode of Tubular Shape

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A tubular flow-through electrode system for measuring the response time curves under the step change of concentration using an ammonium ion-selective poly(vinyl chloride) membrane electrode was described. The response time data are analyzed by the curve fitting method using two theoretical equations, which are an exponential type equation based on an assumption of the film diffusion and a square root type one based on that of the diffusion within the membrane, and a semiempirical equation of hyperbolic type. A method of curve fitting in which the equilibrium potential is regarded as an unknown parameter was described in detail. The initial part of the response time curves, where the potential change is large, was fitted by the exponential type equation, while the following part close to the equilibrium potential was fitted by the square root type one. The semiempirical equation could also be fitted to the wide range of the curves. The dependence of the time constant of the exponential type equation upon the flow rate of sample solution is examined; the results firmly supports both the film diffusion as a determining process for the initial part of the curve and the reliability of the present experimental system.

The discovery of the electrically neutral carrier antibiotics which show the selective complexation behavior toward alkali cations, and the synthesis of the macrocyclic polyethers which show the same behavior as the antibiotics have yielded a large number of ion-selective membrane electrodes of practical use. Among the performance characteristics of these electrodes, the dynamic response behavior is not satisfactorily characterized compared with the selectivity behavior. This is mainly 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), particularly of the order of a few tenths of milliseconds to some seconds, are greatly dependent on the flowing conditions of the bathing solution and are subject to electrical noise. The precise characterization of the response time of ion-selective electrodes is prerequisite for the monitorings in continuous flow-through systems and for the measurements during chemical reactions. Moreover, it is supposed that the investigation of the rate determining processes in the dynamic response of ion-selective electrodes can contribute to the understanding of the electrode response mechanism. Usually the investigation can be done by the curve fitting method using the theoretical equations which predict the response time curves.

In general, to precisely measure response time curves of ion-selective electrodes, it is necessary to control the thickness of the stagnant (adhering) film of the conditioning solution. This is achieved by using simple electrode configurations where the thickness of the stagnant film is straightforward function of the flow rate of the bathing solution. To satisfy this requirement, three geometric types are considered; these are the rotating disk electrode, the so-called wall-jet electrode, and the tubular electrode. Oosterhuis *et al.*[1] applied a rotating disk electrode system to an amperometric flow cell detector for HPLC and continuous flow analysis because the system provided a high sensitivity by controlling the rotation speed. However, to the best of our experience, an application of the rotating disk electrode to the concentration step was unsuccessful, since the sufficiently fast step change was not attained and the measured potential was distorted by electrical noise. Lindner and coworkers[2–5] studied the dynamic chracteristics of precipitate-based electrodes and neutral carrier electrodes using an elaborate apparatus mounted with the solution jets perpendicular to the electrode surface; their apparatus corresponds to the wall-jet electrode system. Akiyama *et al.*[6] also examined the factors affecting the transient response properties of the valinomycin based potassium ion-selective electrode using a wall-jet system, and concluded that the diffusion through a stagnant solution layer was rate controlling. Quite recently, we reported a tubular flow-through electrode system for measuring the response time curves of an ammonium selective poly(vinyl chloride) (PVC) membrane electrode.[7] In the report, we attempted curve fittings using two theoretical equations described by Morf *et al.*[8] The theoretical equations are an exponential type one that based on the assumption of the adhering film diffusion and a square root type one based on that of the diffusion within the membrane. According to Morf *et al.*,[8] the square root type equation essentially explains the dynamic response of carrier membranes. The study by Akiyama *et al.*[6] and our preliminary results,[7] however, suggest that the square root type equation do not always cover the dynamic response behavior of the eletrodes.

The present paper gives a more detailed report dealing with examinations of the curve fitting method and with discussion on the rate determining processes of the dynamic response of the electrode.

Experimental

Chemicals and Membrane Electrode. Macrotetrolide actin mixture (tetranactin 65%, trinactin 30%, dinactin 5%) was kindly supplied by Research Laboratories, Chugai Pharmaceutical Co., Ltd. and was used as ion-selective ligand.[9] The electrode membrane consisted of ligand (5%), dibutyl sebacate (70%, Tokyo Kasei Kogyo Co., Ltd.), and PVC (25%, HS-589, Toyo Soda Manufacturing Co., Ltd.). The tubular

flow-through electrode unit was prepared in the manner mainly after Fraticelli and Meyerhoff.[10] Tygon tubing of internal diameter 0.8 mm was employed as a main part of the tubular electrode. 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.

Apparatus and Procedure. Figure 1 schematically illustrates an experimental set-up for the response time measurement. The tubular membrane electrode (12 in Fig. 1) was attached to the flow system. A silver wire coated with silver chloride (10) was immersed in inner reference solution (11). A conventional silver–silver chloride electrode was placed in the reference electrode compartment (13) containing the waste solution. To eliminate electrical noise, particularly arising from the source of 50 Hz line, a stainless steel pipe (9) was inserted in the upper stream of the tubular electrode, and was connected to the ground terminal of a home made differential impedance converter (5); the terminal was also connected to a shield box made of aluminum chassis which covered the tubular electrode and the reference electrode compartments. A digital storage device (1 on the right in Fig. 1, Auto Digitizer Model 210, Autnics Co., Ltd) provides the resolution of 12-bit, the maximum sampling speed of 1 μs/word, and the storage capacity of 4 Kword. For the acquisition and processing of data, a microcomputer (PC-8801, CPU: μPD780C-1 (Z-80A compatible), 4 MHz, Nippon Electric Co., Ltd.) was used with programmable interfaces μPD8255AC-5 (NEC).

A Liquid drive syringe unit was constructed by attaching a commercial glass syringe (10 ml) to Union Giken Sample Mixing Device MX-7 and connecting Gas Drive Unit-A; a total distance of displacement of the syringe plunger was 40 mm. A linear potentiometer (2 in Fig. 1, Model LP-100F, Midori Precisions Co., Ltd.) was attached to the syringe unit to measure the flow rate of the bathing solution. Another digital storage device with an 8-bit resolution (1 on the left in Fig. 1, Wave Memory Model WM-841, NF Circuit Design Block Co., Ltd.) linked the linear potentiometer to the microcomputer. To interchange the bathing solution, a T-joint for use in HPLC (8) was set as shown in Fig. 1.

In all measurements, 0.1 mol dm^{-3} lithium chloride was used as supporting electrolyte of the bathing solution to eliminate streaming potential between the tubular electrode and the reference electrode compartment. The reason for the use of lithium chloride is that the selectivity coefficient of lithium ion is sufficiently low. Step changes in solution concentrations were attained by closing a cock (6), opening a cook (7), and triggering the gas drive unit to inject new solution into the tubular electrode which had already been exposed to conditioning solution. All measurements were made at room temperature (*ca.* 20 °C).

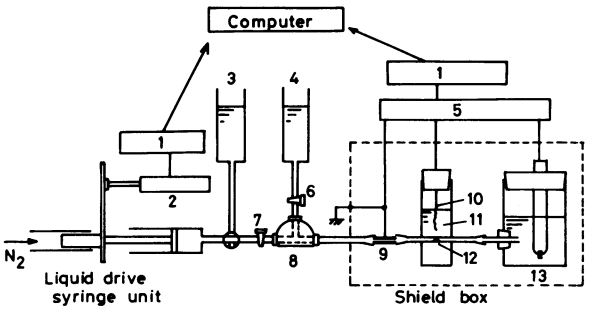

Fig. 1. Experimental set-up for the fast response time measurement.
1: Digital storage device, 2: linear potentiometer, 3: injection solution, 4: conditioning solution, 5: differential impedance converter, 6, 7: two-way stop cocks, 8: T-joint, 9: stainless steel pipe, 10: inner reference electrode (Ag/AgCl), 11: inner solution (NH_4Cl), 12: ion sensitive membrane, 13: reference electrode compartment.

Results and Discussion

As mentioned above, to investigate the rate determining processes in the dynamic response of the ammonium ion-selective electrodes, two theoretical models[8] containing the intrinsic parameters were used for the curve fitting. Additionally, to sufficiently describe the experimental curves, a semiempirical equation was also applied to the curve fitting. The semiempirical equation will be introduced in the following context.

Theoretical Equations. 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:

$$E(t) = E(\infty) + s\log\left[1-\left(1-\frac{a_i^\circ}{a_i}\right)\exp\left(-\frac{t}{\tau'}\right)\right], \quad (1)$$

$$\tau' \approx \frac{\delta^2}{2D'}, \quad (2)$$

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° 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 equation derived from the assumption that the diffusion process within the membrane is regarded as rate controlling:[8]

$$E(t) = E(\infty) = s\log\left[1-\left(1-\frac{a_i^\circ}{a_i}\right)\frac{1}{(t/\tau)^{1/2}+1}\right], \quad (3)$$

$$\tau = \frac{DK^2\delta^2}{\pi D'^2}, \quad (4)$$

where D is the mean diffusion coefficient of electrolyte within the membrane and K is the salt distribution constant.

Curve Fitting Procedure. This paragraph describes a procedure of curve fitting using the exponential type equation; the same procedure can also be applied to the other equations. Our treatment of the least-squares estimate is on the basis of Wentworth's Papers[11,12] and Deming's book[13] dealing with the method of curve fitting applicable to some nonlinear equations. For curve fitting, we rewrite Eq. 1:

$$E(t) = E(\infty) + s\log\left[1-\left(1-\frac{a_i^\circ}{a_i}\right)\exp\left(-\frac{t-\theta}{\tau'}\right)\right], \quad (5)$$

where θ is an time adjustable parameter additionally introduced in order to allow the situation that the theoretical curve do not necessarily pass through the origin of E *vs.* t relationship. In this equation, the unknown parameter to be determined are $E(\infty)$, τ', and θ (but in our previous paper,[7] $E(\infty)$ was regarded as an

experimentally measurable quantity).

The least-squares problem is to determine the three parameters so as to obtain a minimization of the sum of the squares of the residuals:

$$\Sigma[\{E_i(t) - \bar{E}_i(t)\}^2] = \text{minimum}, \tag{6}$$

under the restriction that the condition equations

$$F_i(\bar{t}_i,\ \bar{E}_i(t),\ E(\infty),\ \tau',\ \theta) = \bar{E}_i(t) - E(\infty) - s\log\left[1-\left(1-\frac{a_1^\circ}{a_1}\right)\exp\left(-\frac{\bar{t}_i-\theta}{\tau'}\right)\right] = 0, \tag{7}$$

$$(i = 1,\ 2,\ \cdots\ n)$$

be satisfied. The symbol n is the number of the observed points, $E_i(t)$ is the observed value of the potential, and $\bar{E}_i(t)$ is the adjusted or calculated value of the potential. The weighting factor is treated as equal for all the points. It is assumed that the condition equations are linear with respect to t_i, $E_i(t)$, $E(\infty)$, τ', θ; Eq. 7 are expanded to the first order terms in a Taylor's Series about the point $(t_i, E_i(t), E^\circ(\infty), \tau'^\circ, \theta^\circ)$, where $E^\circ(\infty)$, τ'°, θ° are values of the first approximations. The Taylar's Series expansion and Eq. 6 yield normal equations:

$$\left.\begin{aligned}
&\Sigma\frac{\partial F_i}{\partial E(\infty)}\frac{\partial F_i}{\partial E(\infty)}\Delta E(\infty) + \Sigma\frac{\partial F_i}{\partial E(\infty)}\frac{\partial F_i}{\partial \tau'}\Delta\tau' + \Sigma\frac{\partial F_i}{\partial E(\infty)}\frac{\partial F_i}{\partial \theta}\Delta\theta = \Sigma\frac{\partial F_i}{\partial E(\infty)}F_i^\circ\\
&\Sigma\frac{\partial F_i}{\partial \tau'}\frac{\partial F_i}{\partial E(\infty)}\Delta E(\infty) + \Sigma\frac{\partial F_i}{\partial \tau'}\frac{\partial F_i}{\partial \tau'}\Delta\tau' + \Sigma\frac{\partial F_i}{\partial \tau'}\frac{\partial F_i}{\partial \theta}\Delta\theta = \Sigma\frac{\partial F_i}{\partial \tau'}F_i^\circ\\
&\Sigma\frac{\partial F_i}{\partial \theta}\frac{\partial F_i}{\partial E(\infty)}\Delta E(\infty) + \Sigma\frac{\partial F_i}{\partial \theta}\frac{\partial F_i}{\partial \tau'}\Delta\tau' + \Sigma\frac{\partial F_i}{\partial \theta}\frac{\partial F_i}{\partial \theta}\Delta\theta = \Sigma\frac{\partial F_i}{\partial \theta}F_i^\circ
\end{aligned}\right\} \tag{8}$$

where assuming $\partial F_i/\partial t_i=0$ and $\Delta E(\infty)=E^\circ(\infty)-E(\infty)$, $\Delta\tau'=\tau'^\circ-\tau'$, $\Delta\theta=\theta^\circ-\theta$. This equations can be solved for $\Delta E(\infty)$, $\Delta\tau'$, $\Delta\theta$; the least-square estimates of the parameters $E(\infty)$, τ', θ are calculated. It is usual to repeat the computations using the new $E(\infty)$, τ', θ as the first approximations; setting $E^\circ(\infty)=E(\infty)$, $\tau'^\circ=\tau'$, $\theta^\circ=\theta$, the normal equations 8 are iteratively solved. As a measure of fit, the variance σ^2 is employed:

$$\sigma^2 = \frac{\Sigma\{E_i(t)-\bar{E}_i(t)\}^2}{n-m}, \tag{9}$$

where m is the number of the unknown parameters. Using the new parameters, the variance or the standard error can be calculated. If the iterative procedure results in a satisfactory convergence of the variance, the three parameters are finally determined. Practically, the iterative computations are continued untill the change in σ^2 for successive iterations, $\Delta\sigma^2$, becomes less than a criterion which is previously evaluated by the estimated error in the experiments or some other convenience.

To determine the first approximate values $E^\circ(\infty)$, τ'°, θ°, the following procedure was carried out. The potential at the nearly equilibrium part (*i.e.* at 5 s) on *E-t* curve was employed as the $E^\circ(\infty)$, with which the plot of the left hand function *vs.* t of the linearized equation (from Ep. 5)

$$\ln\frac{1-a_1^\circ/a_1}{1-10^{\{E(t)-E^\circ(\infty)\}/s}} = \frac{1}{\tau'^\circ}t - \frac{\theta^\circ}{\tau'^\circ}, \tag{10}$$

yields the parameters τ'° and θ°.

Results of Curve Fitting. A typical response time curve of the ammonium ion-selective electrode for the concentration change from 1×10^{-4} to 1×10^{-3} mol dm^{-3} ammonium chloride is shown in Fig. 2. The linearized plot of Eq. 10 using 56.1 mV as $E^\circ(\infty)$ is illustrated in Fig. 3. In this example, a straight line is fitted in a range of 60 to 460 ms; the range corresponds to the potential level of 25.9% to 96.8% of the $E^\circ(\infty)$. The correlation coefficient is 0.997.. The lower limit of the range was determined at a flection point of the response time curve; the occurrence of the flection point may due to the unavoidable marginal zone between the conditioning solution and the injection solution. Beyond the range, a deviation notably occurs. The reciprocal slope and the intercept of the fitted straight line determined the values τ'°=158 ms and θ°=40 ms. A result of the iterative procedure with these values is shown in Table 1. As a criterion of $\Delta\sigma^2$, 0.25 (mV)^2 was employed. The $E(\infty)$ gradually approaches the potential of Nernstian response as the successive iteration is continued. Correspondently it is observed that τ' and θ slightly change. The facts that the $E(\infty)$ becomes a reasonable value and that the standard error is sufficiently small (σ=0.8 mV) indicate that this procedure of curve fitting is appropriate for the estimation of the parameters $E(\infty)$, τ', θ. The resultant value τ' will be tried to confirm by examining the flow rate dependence of τ' in the following

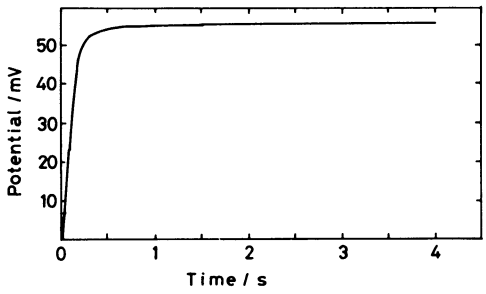

Fig. 2. Typical response time curve for 1×10^{-4} to 1×10^{-3} mol dm^{-3} NH_4Cl. Flow rate is 1.2 m s^{-1}.

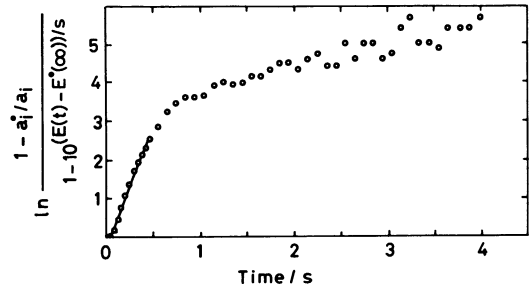

Fig. 3. Linearized plot of the Eq. 10 using the data of Fig. 2. Straight line is fitted in a range of time from 60 to 460 ms.

Table 1. Least-squares adjustment[a] of three parameters of the exponential type equation 5

No.[b]	$E(\infty)$ / mV	τ' / ms	θ / ms	σ^2 [c] / (mV)^2	$\Delta\sigma^2$ [d] / (mV)^2	σ [e] / mV
0	56.1	158	40	2.5	—	1.6
1	56.4	158	43	1.2	−1.3	1.1
2	56.5	158	45	0.7	−0.4	0.9
3	56.5	159	46	0.6	−0.1	0.8

a) Regression range: 60—460 ms. b) Number of iteration. c) Variance. d) The change in σ^2 for successive iterations. e) Standard error.

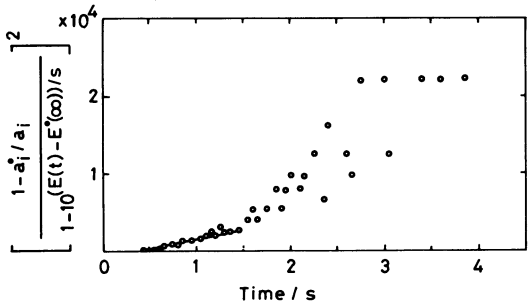

Fig. 4. Linearized plot derived from the square root type Eq. 3 using the data of Fig. 2. Straight line is fitted in a range of time from 480 to 1450 ms.

paragraph. The value θ can be regarded as a time lag due to the marginal zone of the flowing solution.

On the other hand, the linearized plot derived from the square root type equation 3 is shown in Fig. 4. In pratice, we determined the range of regression so that the range should be as wide as possible under the restriction that the correlation coefficient is more than 0.97 for example. The plot is fitted in a range of time from 480 to 1450 ms; the range corresponds to the potential level of 97.3% to 99.3% of the $E^\circ(\infty)$. The correlation coefficient is 0.970. From this linearized plot, τ° and θ° were estimated at 0.33 ms and 457 ms respectively ($E^\circ(\infty)$=56.1 mV). In this case, the iterative computation was carried out only once because the variance immediately converged. As the result, the three parameters were obtained: $E(\infty)$=56.1 mV, τ=0.38 ms, θ=448 ms. The standard error was 0.1 mV. The fact that the lower limit of the fitted range of Eq. 3 is close to the upper limit of the range of the exponential type equation means that the square root time dependence specific to the neutral carrier membrane becomes apparent after the outside equilibration is attained. In this case, the ratio of $\tau'/\tau(\approx D'/(DK^2))$ was about 400. For useful electrode systems, K must be sufficiently less than 1. Accordingly, it seems that the yielded ratio $\tau'/\tau(\approx 400)$ is a reasonable value. If we knew the numerical values D and K in this experimental system, the confirmation of the meaning of τ would be attained. At the present speaking, however, this cannot be done. In the literature,[8] concerning the potassium ion-selective membrane electrode in a fast stirring condition (so-called immersion technique), τ is reported to be 2 ms. Additionally, it is also described that for silcone rubber

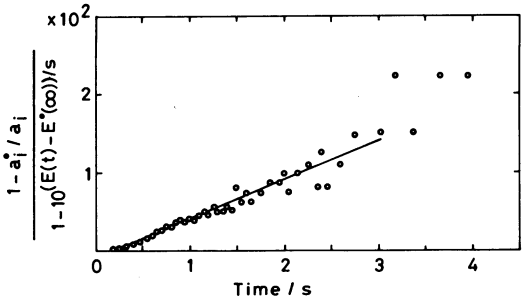

Fig. 5. Linearized plot of the semi-empirical equation using the data of Fig. 2. Straight line is fitted in a range of time from 200 to 3050 ms.

membrane in a rapid flow-through system, τ of down to 1 ms is observed. Under the circumstances, our result of τ=0.38 ms may not be unreasonable. The result of θ=448 ms and upper limit 460 ms of the range of Eq. 1 slightly overlap. In authers' opinion, as mentioned above, the diffusion process within the membrane equivalently begins at the time θ=448 ms. Practically, best fitting by Eq. 1 up to 97% potential completion means the response rate of the electrode is considerably fast. The more precise measurements with this electrode, however, is rather difficult for the diffusion within the membrane.

A Semi-empirical Equation. It seems that a parabola can be fitted to the plot in Fig. 4. This means that instead of Eq. 3 the following equation can be applied to the curve fitting.

$$E(t) = E(\infty) + s\log\left[1-\left(1-\frac{a_i^\circ}{a_i}\right)\frac{1}{t/\tau+1}\right], \tag{11}$$

Accordingly a plotting shown in Fig. 5 was attempted. A straight line can be fitted to the plot in a range of time from 200 to 3050 ms; the range corresponds to the potential level of 83.8% to 99.7% of the $E^\circ(\infty)$. The correlation coefficient is 0.947. The iterative computation yielded the following values: $E(\infty)$=56.2 mV, τ=27.3 ms, θ=165 ms, σ=0.4 ms. As a matter of fact, Eq. 11 can also be derived from the principle of second-order kinetics described by Morf[14] or Buffle and Parthasarathy.[15] According to Morf,[14] the time constant τ of Eq. 11 is equal to $1/(|a_i-a_i^\circ|k)$, where k is the rate constant of an kinetic equation of ion transfer reaction

$$\frac{d}{dt}\Delta a_i(t) = -k[\Delta a_i(t)]^2, \tag{12}$$

$$(\Delta a_i(t) = |a_i'(t)-a_i|).$$

When the potential change is sufficiently small, the logarithmic function in Eq. 11 can be linearized:

$$E(t) = E(\infty) - \frac{1}{At+B}, \tag{13}$$

where A and B are constants. This hyperbolic type expression is equivalent to Müller's equation.[16,17] However, Eq. 11 or 13 is rationalized not for neutral carrier membrane electrodes but for solid-state membrane electrodes (*e.g.* chloride electrode). Therefore the measured time constant τ=27.3 ms is not necessarily to be interpreted by the second-order kinetics mentioned

above.

We cannot theoretically explain why Eq. 11 is more fitted to the data than Eq. 3 is. Qualitatively, the exponential type curve is fast to approach the equilibrium potential, while the square root type curve is slow to do; the hyperbolic type curve has a medium property between the other two equations. In authors' opinion, the setting of $E°(\infty)$ is just appropriate to the curve fitting with Eq. 11. In our treatment, the potential at 5 s was employed as $E°(\infty)$ and the range of observation was restricted up to 4 s. If the Eq. 3 is forced to be fitted to the potential at about 4 s, the equilibrium potential should be higher than the potential at 5 s. At present, we can only say that the semi-empirical equation (Eq. 11) is apparently fitted to the data if the potential at several seconds is taken as equilibrium potential.

Effect of Flow Rate. A remarkable character of our apparatus is that the thickness of the adhering layer can be controlled by varying the flow rate. The flow rate was varied from 1.1 to 2.6 m s^{-1}. This corresponds to the Reynolds number from 860 to 2040. The flow of fluid in a smooth pipe at Reynolds numbers up to about 2000 is always laminar. If the wall of our tubular electrodes, however, have rough surface, the turbulent flow may occurs. Therefore we must examine both the cases of the laminar flow and the turbulent flow. For the turbulent flow in a smooth pipe, the thickness of adhering layer δ is expressed as a function of the flow rate of sample solution:[18]

$$\delta = (\text{const})v^{-7/8}, \tag{14}$$

where v is the linear flow rate and (const) is a lumped constant. By eliminating δ from Eqs. 2 and 14, a theoretical relationship between τ' and v is derived:

$$\tau' = (\text{const})'v^{-7/4}, \tag{15}$$

where (const)′ is a lumped constant. On the other hand, assuming the laminar flow, $\tau' \propto v^{-2/3}$. Figure 6 shows a log-log plot of τ' against v using the data for concentration change from 1×10^{-4} to 1×10^{-3} mol dm^{-3} NH_4Cl. In this case, every upper limit of the range of regression is fixed on 97% of completion of potential response. The slope of the straight line drawn through the experimental points is −1.3; the correlation coefficient is 0.973. A series of the experimental data is located between the turbulent domain and the laminar domain, but is rather close to the turbulent one. In this paragraph, the flow rate dependence of the time constants are discussed; but the absolute values of the time constants are not confirmed yet. The facts that the initial part of the response time data was best fitted by Eq. 1 and that the flow rate dependence of the time constants was approximately agree with the expectation assuming the turbulent flow, however, support the assumption that the initial part of the response time data is due to the film diffusion.

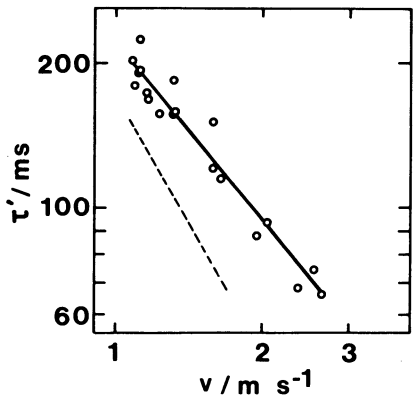

Fig. 6. Log-log plot of the time constant τ'(in Eq. 15) against the linear flow rate v using the data for concn change from 1×10^{-4} to 1×10^{-3} mol dm^{-3} NH_4Cl. The full line is drawn through the points; the slope is −1.3. The broken line represents a theoretical slope (−1.75). Every upper limit of the range of regression is 97% of completion of potential response.

Theoretically the dependence of the square root type equation (Eq. 3) upon the flow rate is the same with that of the exponential type one (refer to Eqs. 2 and 4). Actually, the slope of log-log plot of τ in Eq. 3 against v using the same data that was described above was also close to the theoretical one. The range of regression was from 97% to 99%. But the correlation coefficient was considerably less than that of Fig. 6. This is due to the fact that the effect of experimental error becomes relatively large because of the slightly variation in potential.

Conclusion

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. For the curve fitting, two theoretical equations and a semi-empirical equation were used. A method of curve fitting in which the equilibrium potential was regarded as an unknown parameter provided reasonable results concerning the time constant, the equilibrium potential, and the adjustable parameter of time. On the response time curves, the first part where the potential change is large was fitted by the theoretical equation based on the film diffusion, while the next part close to the equilibrium potential was fitted by that based on the diffusion process within membrane. On the other hand, a semi-empirical equation of hyperbolic type could also be fitted to the wide range of the response time curves.

The fact that the dependence of the time constant of the exponential type equation upon the flow rate was fairly consistent with the theoretical expectation supports both the explanation of the first part of the response time curves by means of the film diffusion and the reliablity of the present experimental system.

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