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Flux and Characteristic Parameters in Mediated Transport through Liquid Membranes. II. A Model for Co-transport and Experimental Study of KI Transport through a Bulk Liquid Membrane

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Abstract

In this article we establish a steady-state theoretical model for cotransport through liquid membranes. Integration of the flux equation gives the concentration in the receiving phase as a linear function of time under certain conditions. From this, an expression for the relative permeability of the carrier–permeant complex with respect to the carrier is obtained; this permeability depends on the equilibrium constant of the interphases reaction and on another parameter related to the initial concentration of permeant in extramembrane phases. An experimental study of the variation of permeant concentration in the receiving phase allows determination of several characteristic transport parameters.

INTRODUCTION

In a previous paper published in this *Journal* (*1*), a steady-state mathematical model was established for simple-carrier mediated transport in liquid membranes. In this paper the model is extended to the coupled carrier-mediated transport or cotransport. In this case the permeant, an ionic species, is transported by a carrier which can bind to both the positive and negative ions by the formation of an neutral complex, which can diffuse freely within the membrane. A laboratory study for KI transport through a chloroform liquid membrane, with dibenzo 18 crown 6 (DB18C6) as carrier, is carried out; the results and the model lead to the determination of some characteristic transport parameters, such as the permeability in the membrane corresponding to the carrier and to the carrier-permeant complex.

COTRANSPORT MODEL DESCRIPTION

The liquid membrane transport needs a chemical carrier (B) inside the membrane (C_T, total concentration), given that the permeant, an ionic species in aqueous solution, cannot enter the membrane because the membrane consists of a hydrophobic organic solvent which rejects ion because they have very low soluability. B reacts with the permeant at one of the interfaces, transports it through the membrane, and releases it at the other interface. If we denote the permeant AC (A^-, anion; C^+, cation), the mechanism proposed for the process is

$$A + B + C \rightleftharpoons ABC$$

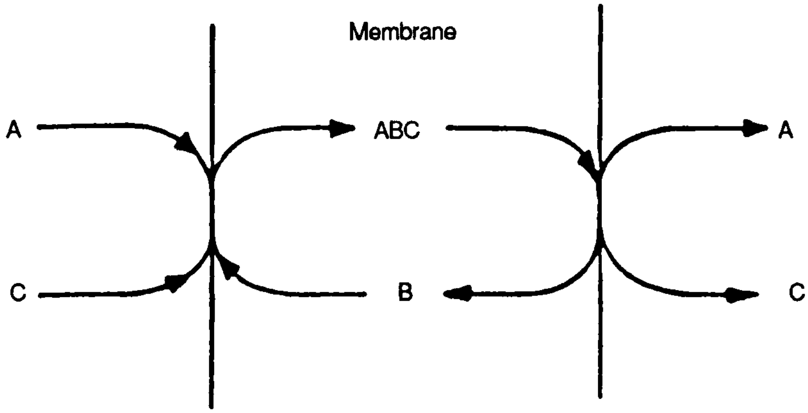

FIG. 1. Simplified representation of the cotransport of permeate AC by the active carrier B.

schematically shown in Fig. 1, and where ABC is the carrier–permeant complex.

We assume that the carrier in either the free or complex form cannot leave the membrane, and so the total amount of carrier in the system is conserved. In this way, we take as a basic hypothesis that

$$C_{\mathrm{T}} = C_{\mathrm{B}} + C_{\mathrm{ABC}} \tag{1}$$

where C_{B} and C_{ABC} are the concentrations of B and ABC, respectively.

We will only treat the steady-state situation (in some cases this assumption may be inappropiate due to thick membranes or slow interfaces reaction rates). With this restriction, the concentrations of ABC at the interfaces are

$$\begin{aligned} C_{\mathrm{ABC}}^{s} &= \frac{k_e C_{\mathrm{A}}^{s} C_{\mathrm{C}}^{s} C_{\mathrm{T}}}{1 + k_e C_{\mathrm{A}}^{s} C_{\mathrm{C}}^{s}} \\ C_{\mathrm{ABC}}^{r} &= \frac{k_e C_{\mathrm{A}}^{r} C_{\mathrm{C}}^{r} C_{\mathrm{T}}}{1 + k_e C_{\mathrm{A}}^{r} C_{\mathrm{C}}^{r}} \end{aligned} \tag{2}$$

where the superscripts s and r refer to the source and receiving phases, respectively ($C_{\mathrm{A}}^{s} > C_{\mathrm{A}}^{r}$), and k_e is the equilibrium constant of the reaction at the interfaces.

The mediated flux, when A and C are ions that correspond to the saline flux, is defined as the number of moles of AC incorporated in the receiving phase/time, and is given by

$$\begin{aligned} J &= P_{\mathrm{ABC}}(C_{\mathrm{ABC}}^{s} - C_{\mathrm{ABC}}^{r}) \\ &= \frac{J_{\max}\,(C_{\mathrm{A}}^{s} C_{\mathrm{C}}^{s} - C_{\mathrm{A}}^{r} C_{\mathrm{C}}^{r})}{(1 + k_e C_{\mathrm{A}}^{s} C_{\mathrm{C}}^{s})(1 + k_e C_{\mathrm{A}}^{r} C_{\mathrm{C}}^{r})} \end{aligned} \tag{3}$$

where $J_{\max}$ is the maximum initial flux:

$$J_{\max} = P_{\mathrm{ABC}} C_{\mathrm{T}} \tag{4}$$

with P_{ABC} the apparent permeability of ABC through the membrane. In the initial flux conditions ($C_{\mathrm{A}}^{r} = C_{\mathrm{C}}^{r} = 0$), Eq. (3) reduces to

$$J_0^{\uparrow} = J_{\max} k_e \, \frac{C_{\mathrm{A}}^{s} C_{\mathrm{C}}^{s}}{1 + k_e C_{\mathrm{A}}^{s} C_{\mathrm{C}}^{s}} \tag{5}$$

We will consider the transport of a strong electrolyte of type 1:1, so that $C^r_A = C^r_C = C^r$ and $C^s_A = C^s_C = C^s$, and Eqs. (3) and (5) become

$$J = \frac{k_e[(C^s)^2 - (C^r)^2]J_{\text{max}}}{[1 + k_e(C^s)^2][(1 + k_e(C^r)^2]} \tag{6a}$$

$$J_0^{\dagger} = J_{\text{max}} k_e \frac{(C^s)^2}{1 + k_e(C^s)^2} \tag{6b}$$

Equations (3)–(6) are valid when the carrier permeability (P_B) is equal to P_{ABC}. In the general case, $P_B \neq P_{ABC}$ and we will establish an expression for the flux J from the following assumptions:

i) In steady-state, the number of carriers moving from the source phase to the receiving phase must be equal to the number moving in the opposite direction. Therefore:

$$P_{ABC}C^s_{ABC} + P_B C^s_B = P_{-ABC}C^r_{ABC} + P_{-B}C^r_B \tag{7}$$

Assuming that $P_{ABC} = P_{-ABC}$ and $P_B = P_{-B}$, Eq. (7) reduces to

$$\rho[C^s_{ABC} - C^r_{ABC}] = C^r_B - C^s_B \tag{8}$$

with

$$\rho = P_{ABC}/P_B \tag{9}$$

ii) From Eq. (1) it follows that

$$C^s_B + C^r_B + C^s_{ABC} + C^r_{ABC} = 2C_T \tag{10}$$

On the other hand, Eqs. (2), which are valid in every case, can be written in the form

$$k_\alpha = \frac{C^r_A C^r_B C^r_C}{C^r_{ABC}} = \frac{(C^r)^2 C^r_B}{C^r_{ABC}} \tag{11a}$$

$$k_\alpha = \frac{C^r_A C^r_B C_C}{C^r_{ABC}} = \frac{(C^r)^2 C^r_B}{C^r_{ABC}} \tag{11b}$$

where $k_\alpha = 1/k_e$ when $C^s_A = C^s_B = C^s$ and $C^r_A = C^r_B = C^r$.

From Eqs. (11), one can deduce C_B^s and C_B^r, whose expressions, when carried to Eqs. (8) and (10), give rise to a system of equations from which C_{ABC}^r and C_{ABC}^s can be inferred. So,

$$C_{ABC}^s = \frac{2C_T(C^s)^2}{\Delta}[k_\alpha + \rho(C^r)^2] \tag{12}$$

with

$$\Delta = [k_\alpha + (C^s)^2][k_\alpha + \rho(C^r)^2] + [k_\alpha + (C^r)^2][k_\alpha + \rho(C^s)^2] \tag{13}$$

and

$$C_{ABC}^r = C_{ABC}^s \frac{k_\alpha + \rho(C^s)^2}{k_\alpha + \rho(C^r)^2}\left[\frac{C^r}{C^s}\right]^2 \tag{14}$$

In this way the flux is given by

$$J = P_{ABC}C_T k_\alpha \frac{2}{\Delta}[(C^s)^2 - (C^r)^2] \tag{15}$$

Equation (15) reduces to Eq. (6a) by making $\rho = 1$ and taking into account Eq. (4).

1. Integration of the Flux Equation

The next objective is the integration of Eq. (15) in the steady-state situation, given two point boundary conditions on permeant concentrtions at the two membrane interfaces. We denote C_0^s and C_0^r as the initial concentrations ($t = 0$) in the source and receiving phases, respectively. At any given instant the following equation applies (*1*):

$$C^s = C_0 - v_r C^r \tag{16}$$

with

$$C_0 = C_0^s + v_r C_0^r - v_m \bar{C}_{ABC} \tag{17}$$

where $\bar{C}_{\mathrm{ABC}}$ is the mean concentration of ABC at the membrane, which in steady-state has a constant value; ν_r is the quotient of the receiving phase volume (V_r) and the source phase (V_s):

$$\nu_r = V_r/V_s \tag{18}$$

while ν_m is the relative volume of the membrane (volume V_m) with respect to the source phase, $\nu_m = V_m/V_s$. Under certain conditions that we assume ($\bar{C}_{\mathrm{ABC}}$ value very small in comparison with C_0^s and C_0^r, and so $\bar{C}_{\mathrm{ABC}}\nu_m$ may be suppressed in Eq. 17), or in the case of thin membranes ($V_m \ll V_s$ and V_r), then

$$C_0 = C_0^s + \nu_r C_0^r \tag{19}$$

When $\nu_m = 1$, C_0 is equal to the sum of the permeant initial concentrations in the extramembrane phases.

In every case, J is given by

$$J = V_r \frac{dC^r}{dt} = -V_s \frac{dC^s}{dt} \tag{20}$$

The integration of this equation, taking into account Eq. (15) and assuming an initial permeant concentration at the receiving phase equal to zero ($t = 0$, $C_0^r = 0$), permits us to obtain the variation of C^r with time.

The integral to be calculated is of the form

$$\int_0^t dt = V_r C_0 \int_0^{\hat{C}^r(t)} dz/J(z) \tag{21}$$

where $z = \hat{C}^r(t) = C^r(t)/C_0$. From Eqs. (15), (16), and (21) it follows that

$$J_m \frac{t}{V_r} = \int_0^{\hat{C}^r} [P_4(z)/P_2(z)]dz \tag{22}$$

where $J_m = 2C_{\mathrm{T}}P_{\mathrm{ABC}}k_\alpha$, $P_4(z)$ and $P_2(z)$ are two polynomials of 4th and 2nd degree, respectively, i.e.,

$$\begin{aligned} P_4(z) &= az^4 + bz^3 + cz^2 + dz + e \\ P_2(z) &= \alpha z^2 + \beta z + \gamma \end{aligned} \tag{23}$$

with

$$\begin{aligned} a &= 2\rho C_0^4 \nu_r^2;\ b = -4\rho C_0^4 \nu_r;\ C = (1 + \nu_r^2)(1 + \rho)k_\alpha^2 + 2\rho C_0^4 \\ d &= -2k_\alpha C_0^2 \nu_r (1 + \rho);\ e = 2k_\alpha^2 + k_\alpha C_0^2(1 + \rho) \end{aligned} \tag{24}$$

$$\alpha = (\nu_r^2 - 1)C_0;\ \beta = -2\nu_r C_0;\ \gamma = C_0 \tag{25}$$

so that

$$\frac{P_4(z)}{P_2(z)} = 3a_3 z^3 + 2a_2 z^2 + a_1 z + \frac{pz + q}{P_2(z)} \tag{26}$$

where

$$\begin{aligned} a_3 &= (2/3)\rho C_0^3 \nu_r^2/(\nu_r^2 - 1);\ a_2 = 2\rho C_0^3/\nu_r^2 - 1)^2 \\ a_1 &= [(1 + \nu_r^2)(\nu_r^2 - 1)^2(1 + \rho)k_\alpha C_0 + 2\rho C_0^3(3\nu_r^2 + 1)]/(\nu_r^2 - 1)^3 \end{aligned} \tag{27}$$

$$p = [4k_\alpha C_0^2(1 + \rho)\nu_r(\nu_r^2 - 1)^2 + 8\rho\nu_r C_0^4(\nu_r^2 + 1)]/(\nu_r^2 - 1)^3 \tag{28}$$

and

$$\begin{aligned} q = {} & [2k_\alpha^2(\nu_r^2 - 1)^3 - 2k_\alpha C_0^2(1 + \rho)(\nu_r^2 - 1)^2 \\ & - 2\rho C_0^4(3\nu_r^2 + 1)]/(\nu_r^2 - 1)^3 \end{aligned} \tag{29}$$

This equation, carried to Eq. (22), leads to

$$\frac{J_m t}{V_r} = a_3(\hat{C}^r)^3 + a_2(\hat{C}^r)^2 + a_1\hat{C}^r + \int_0^{\hat{C}^r} \frac{pz + q}{P_2(z)}\,dz \tag{30}$$

As

$$\begin{aligned} P_2(z) &= C_0(\nu_r^2 - 1)\left[z^2 - \frac{2\nu_r}{\nu_r^2 - 1}z + \frac{1}{\nu_r^2 - 1}\right] \\ &= C_0(\nu_r^2 - 1)(\theta^2 - A^2) \end{aligned} \tag{31}$$

with

$$\theta = z - \frac{\nu_r}{\nu_r^2 - 1}\,;\; A = \frac{1}{\nu_r^2 - 1} \tag{32}$$

the integral of Eq. (30) becomes

$$\int_0^{\hat{C}^r} \frac{pz + q}{P_2(z)} dz = \frac{1}{C_0(\nu_r^2 - 1)} \int_{\theta_0}^{\theta} \frac{P\theta + Q}{\theta^2 - A^2} d\theta \tag{33}$$

with

$$\theta_0 = -\nu_r/(\nu_r^2 - 1);\; P = p;\; Q = q + [p\nu_r/(\nu_r^2 - 1)] \tag{34}$$

Integrating in Eq. (33), Eq. (30) reduces to

$$\begin{aligned} J_m t/V_r = {} & a_3[\hat{C}^r(t)]^3 + a_2[\hat{C}^r(t)]^2 + a_1\hat{C}^r(t) \\ & + \frac{1}{C_0(\nu_r^2 - 1)} \Big[(P + Q') \ln [1 - (\nu_r - 1)\hat{C}^r(t)] \\ & + (P - Q') \ln [1 - (\nu_r + 1)\hat{C}^r(t)]\Big] \end{aligned} \tag{35}$$

where

$$Q' = Q/A = p\nu_r + q(\nu_r^2 - 1) \tag{36}$$

For values of $\hat{C}^r \ll 1$ (initiation of the experiment), we can disregard terms greater than first order in the polynomial part of Eq. (35) and expand the Napierian logarithms in the McLaurin series, and so Eq. (35) becomes

$$\frac{J_m t}{V_r} \cong \left[a_1 + \frac{P^{\nu}_r - Q'}{C_0(\nu_r^2 - 1)}\right] \hat{C}^r(t) \tag{37}$$

This equation shows the linear behavior of $\hat{C}^r(t)$ vs t in the conditions considered. Taking into account that

$$\frac{P\nu_r - Q'}{C_0(\nu_r^2 - 1)} = -\frac{q}{C_0} \tag{38}$$

with q from Eq. (29), Eq. (37) gives

$$J_m t/V_r = \hat{C}^r(t)\delta/(\nu_r^2 - 1) \tag{39a}$$

with

$$\delta = (1 + \nu_r^2)(1 + \rho)k_\alpha C_0 + \frac{2k_\alpha^2}{C_0}(\nu_r^2 - 1) - 2k_\alpha C_0(1 + \rho) \tag{39b}$$

from which

$$\hat{C}^r(t) = \frac{C^r(t)}{C_0} = \frac{1}{V_r}(\nu_r^2 - 1)\frac{1}{\delta}J_m t \tag{40}$$

Deriving with respect to t:

$$\frac{dC^r(t)}{dt} = \frac{C_0 J_m t(\nu_r^2 - 1)}{V_r\delta} \tag{41}$$

In carrier saturation conditions:

$$J = J_{\max} = V_r \lim_{t\to 0}(dC^r/dt) = V_r\alpha \tag{42}$$

where α is the slope of the function $C^r = C^r(t)$ for $t = 0$. In these conditions, $J_m = 2J_{\max}k_\alpha = 2V_r\alpha k_\alpha$, and from Eq. (41) it follows for $t \to 0$ that

$$1 = 2C_0 k_\alpha(\nu_r^2 - 1)/\delta \tag{43}$$

Deducing ρ:

$$\rho = 1 - (2k_\alpha/C_0^2) \tag{44}$$

a result that is independent of ν_r.

Alternatively, a full study may be accomplished for $\nu_r = 1$, resulting in

$$\frac{J_m t}{V_r} = \alpha_4(\hat{C}^r)^4 + \alpha_3(\hat{C}^r)^2 + \alpha_2(\hat{C}^r)^2 + \alpha_1(\hat{C}^r) - \frac{\alpha_0}{2C_0}\ln(1 - 2\hat{C}^r) \tag{45}$$

with

$$\alpha_4 = -\rho C_0^3/4;\ \alpha_3 = -2\alpha_4;\ \alpha_2 = -[k_\alpha(1+\rho) - \alpha_4]/2$$
$$\alpha_1 = [k_\alpha C_0(1+\rho) + \alpha_4]/2;\ \alpha_0 = 2k_\alpha^2 + C_0(\alpha_1 - \alpha_4) \tag{46}$$

For values of $\hat{C}^r \ll 1$,

$$\hat{C}^r(t) = \frac{2J_{\max}t}{V_r C_0\left(1 + \rho + \dfrac{2k_\alpha}{C_0}\right)} \tag{47}$$

which, in saturation carrier conditions, also reduces to Eq. (43).

As $P_{ABC} \leqslant P_B$, due to the greater size of complex ABC face to B, then $0 \leqslant \rho < 1$, and the following condition for the transport is obtained:

$$0 < k_\alpha/C_0^2 \leqslant 1 \rightarrow 0 < C_B \leqslant C_{ABC}/2 \tag{48}$$

because, in the situation considered, $k_\alpha \cong (C_B/C_{ABC})C_0^2$. Equation (48) establishes that in every case the free carrier concentration must be less or equal to half of the carrier-permeant complex concentration. If $k_\alpha \ll C_0$, $\rho = 1$ and $P_B = P_{ABC}$.

The above results show the conditions for the accomplishment of mediated cotransport through a liquid membrane in the steady-state situation considered, and allows us to determine ρ, P_B, and P_{ABC} from the experimental study of $C^r(t)$.

EXPERIMENTAL

1. Reactor

The membrane used was made of chloroform containing DB18C6 (Fluka purum) as carrier. The total concentration of DB18C6 in chloroform was 10^{-2} mol/L. The carrier solution (200 cm^3) was located at the bottom of a thermostated cell (reactor in Fig. 2). A glass bell cylinder, joined to the reactor cover and suspended above the bottom of the reactor,

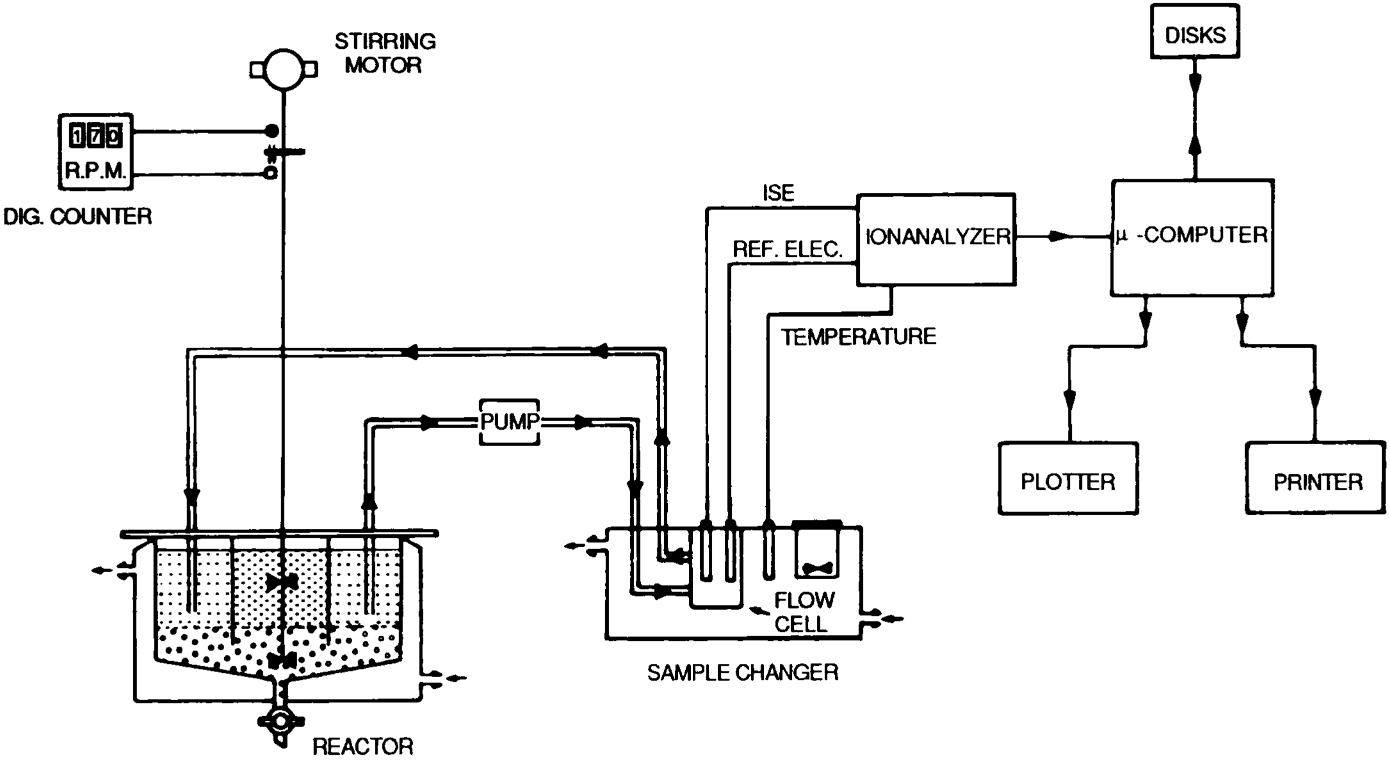

FIG. 2. Schematic diagram of the experimental device.

separated the inner aqueous phase (source phase; V_s = 170 cm^3) and the outer aqueous phase (receiving phase; V_r = 260 cm^3). These aqueous phases are aqueous solutions of KI (Merck suprapur), with initial concentrations $C_0 = 1\ M$ and $C_0 = 5 \times 10^{-3}\ M$, prepared with degased, deionized, and bidistilled water. The membrane is stirred by means of a propeller with controlled speed, while the aqueous phases are stirred by recirculation. The reactor is thermostated by a thermal circuit that can be used for both heating and cooling. The experiment was conducted at 25.5 ± 0.1°C.

2. Measurement System

To measure concentration changes in the receiving phase, an ISE for I^- (Orion, model 94-53BN) was used with a double-union reference electrode (Orion, model 90-02). Because electrodes require periodic calibration, we designed a sample changer thermostated in parallel with the reactor, with six magnetic stirring vessels for standard solutions, one of which also acts as a wash vessel, and a flow cell in which the electrodes are placed (*2*). The electrode response is fed to an ionanalyzer (Orion, EA940) where the temperature, the concentration, and the associated electrical potential difference are displayed in continuous form. By means of an output RS232C, the data obtained are sent to a microcomputer where they are stored for further use (Fig. 2).

3. Data Acquisition and Recording System (*2*)

An informatic system is used for acquiring, storing, and processing the data. This system consists of a microcomputer (Olivetti M24) with three RS232C interfaces, a high resolution graphics screen, a printer (Olivetti DM 286/2), and a plotter (Roland DXY 880); the operating system is a MS-DOS. A first program automatically collects the measurements carried out by the ionanalyzer. When these data make up a complete measurement, the program stores and displays it on the screen. The transmission of this information can be interrupted at any time so that additional information can be entered through the keyboard or electrode calibrations can be carried out.

A second program facilitates the management of the data stored by the first program, and its task is to list and display graphically the measurements obtained. When a file name is given by the user, this program enables him to extract the file and see the characteristic parameters of the process and the values of measurements at specific times, generating a total or partial listing and a graphic representation of the measurements. Alternatively, a copy can be obtained by a printer or a plotter.

RESULTS

The permeant concentration in the receiving phase was measured in a continuous way. Figure 3 illustrates the variation of this concentration as a function of time (the arrows indicate points of calibration). The linear behavior shows the validity of Eq. (44), from which a value of 0.74 for ρ is obtained (for the k_α value, see Ref. *3*). Because the maximum flux J_{max} is given by Eq. (4) and corresponds to the slope of $C(t)$ ($\alpha = 1.75 \times 10^{-3}$ mol · L^{-1} · h^{-1}) multiplied by the volume V_r for $t \to 0$, from Fig. 3 it follows that

$$J_{\text{max}} = 0.455 \times 10^{-3} \text{ mol/h} = 7.58 \times 10^{-6} \text{ mol/min} \qquad (49)$$

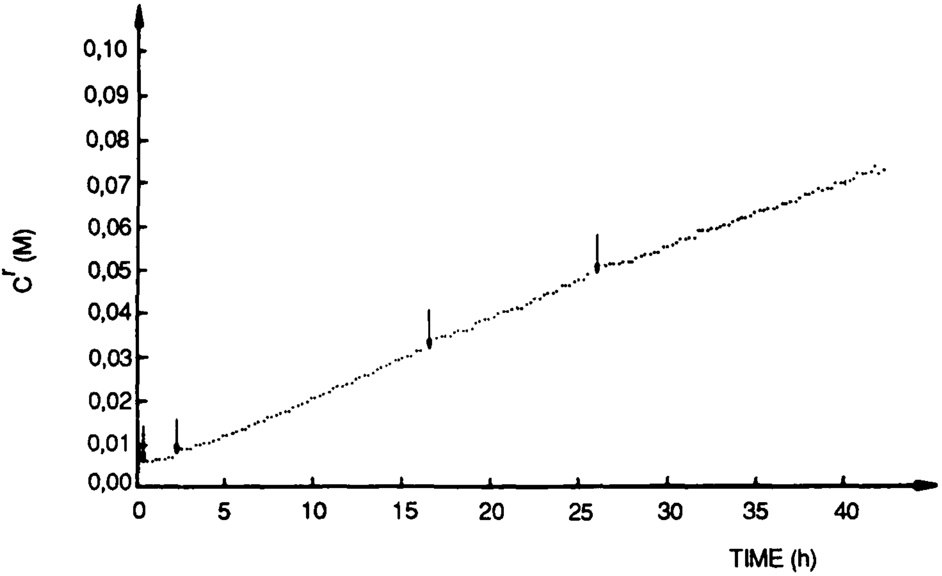

FIG. 3. Electrodic concentration measurement in the receiving phase. The arrows show electrode calibrations.

from which

$$P_B = 12.63 \times 10^{-3}\ \text{cm/s},\ P_{ABC} = 9.35 \times 10^{-3}\ \text{cm/s}$$

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