Relaxation Times for Build-up & Decay of Electroosmotic Pressure & for Build-up of Streaming Potential

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Received 22 August 1979; accepted 12 November 1979

The irreversible thermodynamic membrane transport theory of electrokinetic phenomena has been used to predict the relaxation times for the build-up and decay of electroosmotic pressure and the build-up of streaming potential. To test the validity of the derived equations, build-up and decay of electroosmotic pressure and build-up of streaming potential have been experimentally determined for Amberlite IRC (50) membrane/methanol system and Zeokarb 225 membrane/methanol system respectively. Relaxation times have also been estimated from the hydrodynamic flux data for comparison.

Theory

According to the theory of irreversible thermodynamics of electrokinetic membrane transport phenomena, the volumetric flux, $J$, and electric current, $I$, under the simultaneous action of hydrodynamic pressure difference, $\Delta P$, and electrical potential difference, $\Delta \phi$, may be expressed by Eqs. (1) and (2).

$$J = L_{11} \frac{\Delta P}{T} + L_{12} \frac{\Delta \phi}{T} \quad (1)$$

$$I = L_{21} \frac{\Delta P}{T} + L_{22} \frac{\Delta \phi}{T} \quad (2)$$

where $L$'s are phenomenological coefficients subject to the restrictions:

$$L_{12} = L_{21}; \quad L_{12} < L_{11} \quad L_{22} \quad (3)$$

Using Equations (1) and (2) on rearrangement give the following relations for various steady states.

(i) Electroosmotic flow:

$$\left( J_{\Delta \phi=0} \right) = L_{12} \left( \frac{\Delta \phi}{T} \right) \frac{I}{J} \quad \Delta P = 0 \quad L_{12} \quad (4)$$

(ii) Hydrodynamic flow:

$$\left( J_{\Delta \phi=0} \right) = L_{11} \left( \frac{\Delta P}{T} \right) \quad (5)$$

(iii) Electroosmotic pressure:

$$\left( \Delta P_{\Delta \phi=0} \right) = - \frac{L_{13}}{L_{11}} \Delta \phi \quad (6)$$

(iv) Electrical conductance:

$$\left( \frac{I}{\Delta \phi} \right)_{\Delta \phi=0} = \frac{L_{22}}{T} \quad (7)$$

(v) Streaming current:

$$\left( I_{\Delta \phi=0} \right) = L_{21} \left( \frac{\Delta P}{T} \right) \frac{I}{J} \quad \Delta \phi = 0 \quad L_{21} \quad (8)$$

(vi) Streaming potential:

$$\left( \Delta \phi_{I=0} \right) = - \frac{L_{21}}{L_{22}} \Delta P \quad (9)$$

These steady states are interrelated on account of Onsager's reciprocity relation as:

$$\left( \frac{\Delta \phi}{\Delta P} \right)_{I=0} = - \left( \frac{I}{J} \right)_{\Delta \phi=0} \quad (10)$$

$$\left( \frac{\Delta \phi}{\Delta P} \right)_{I=0} = - \left( \frac{J}{I} \right)_{\Delta \phi=0} \quad (11)$$

The time required for the build-up and decay of the electrical double layer, responsible for the occurrence of electroosmotic effects, is given by:

$$t \sim \frac{a^2 \mu}{\eta} \quad (12)$$
where, \( a \) is the average pore radius of the membrane and \( \eta \) is the coefficient of viscosity of the permeant having density \( \rho \). The average pore radius of the membranes under investigation, estimated from the hydrodynamic permeability and equilibrated membrane conductance data employing the method suggested by Kumar, is of the order of \( 10^{-4} \) cm. For water, \( t \approx 10^{-4} \) sec, which clearly indicates that electroosmotic flow \((J)_{\Delta \phi = 0}\) can be assumed time invariant. Hence, the relaxation time is determined by the induced hydrodynamic flow \((J)_{\Delta \phi = 0}\). 

**Electroosmotic pressure** — In the electroosmotic pressure experiment, counter pressure generated by electroosmotic displacement of the liquid causes hydrodynamic flow of the liquid in the opposite direction. At any instant, one may therefore, write the net flow, \( J \), as:

\[
(J)_{\tau} (t) = (J)_{\Delta \phi = 0} - (J)_{\Delta \phi = 0} (t) \quad \text{(13)}
\]

Steady electroosmotic pressure is obtained when \((J)_{\tau} (\infty) = 0\), or

\[
(J)_{\Delta \phi = 0} = (J)_{\Delta \phi = 0} (\infty) \quad \text{(14)}
\]

so that Eq. (13) may be expressed as,

\[
(J)_{\tau} (t) = (J)_{\Delta \phi = 0} (\infty) - (J)_{\Delta \phi = 0} (t) \quad \text{(15)}
\]

If radius of the electroosmotic pressure measuring capillary is \( r \), we may write using phenomenological relation (5) and Eq. (15),

\[
\pi r^2 \frac{d}{dt} (\Delta P) (t) = \frac{L_{11}}{T} (\Delta P) (\infty) - \frac{L_{11}}{T} (\Delta P) (t) \quad \text{(16)}
\]

or

\[
\frac{d}{dt} (\Delta P) (t) - (\Delta P) (\infty) = \frac{L_{11}}{T \pi r^2} \cdot dt \quad \text{(17)}
\]

Integration of Eq. (17) using the boundary condition \( \Delta P = 0 \) when \( t = 0 \), yields,

\[
(\Delta P) (t) = (\Delta P) (\infty) [1 - \exp (-L_{11}/T \pi r^2) t] = (\Delta P) (\infty) [1 - \exp (-t/\tau_\star)] \quad \text{(18)}
\]

where, \( \tau_\star = \frac{T \pi r^2}{L_{11}} \quad \text{(19)} \)

\( \tau_\star \) is the relaxation time, the time required for the electroosmotic pressure to rise \( (1 - \frac{1}{e}) \) of its steady value.

During decay of the electroosmotic pressure, \((J)_{\Delta \phi = 0} = 0\). It, therefore, follows from Eq. (13) that

\[
(J)_{\tau} (t) = - (J)_{\Delta \phi = 0} (t) \quad \text{(20)}
\]

or

\[
\frac{d}{dt} (\Delta P) (t) - (\Delta P) (\infty) = \frac{L_{11}}{T \pi r^2} \cdot dt \quad \text{(21)}
\]

On integration using the boundary condition, \( \Delta P = (\Delta P) (\infty) \), when \( t = 0 \), we find that,

\[
(\Delta P) (t) = (\Delta P) (\infty) e^{-t/\tau_\star} \quad \text{(22)}
\]

Equations (18) and (22) show the time-dependent build-up and decay of electroosmotic pressure respectively.

**Streaming potential** — When a liquid is forced through a membrane, migration of ions of the diffused part of electrical double layer occurs. This leads to accumulation of charges of opposite sign on the two faces of the membrane. The generated electric field produces an electromigration current of ions in the opposite direction such that at any instant,

\[
(I)_{\tau} (t) = (I)_{\Delta \phi = 0} - (I)_{\Delta \phi = 0} (t) \quad \text{(23)}
\]

At the steady state, streaming current and electromigration current are balanced, a stationary electrical potential, \((\Delta \phi)_{\tau = 0}\), called streaming potential is established so that,

\[
(I)_{\Delta \phi = 0} = (I)_{\Delta \phi = 0} (\infty) = \frac{(\Delta \phi) (\infty)}{R} \quad \text{(24)}
\]

where \( R \) is the resistance of the membrane equilibrated with the permeant. Equation (23) may therefore, be written as,

\[
(I)_{\tau} (t) = \frac{(\Delta \phi) (\infty)}{R} - \frac{(\Delta \phi) (t)}{R} \quad \text{(25)}
\]

The current \((I)_{\tau} (t)\) during streaming may be detected with an electrometer. We may write,

\[
(I)_{\tau} (t) = \frac{d}{dt} Q(t) = C \frac{d}{dt} ((\Delta \phi) (t)) \quad \text{(26)}
\]

where \( C \) is the electrometer capacitance. Thus it follows from Eq. (25) that,

\[
\frac{d (\Delta \phi) (t)}{(\Delta \phi) (\infty) - (\Delta \phi) (t)} = \frac{dt}{R C} \quad \text{(27)}
\]

Integration of Eq. (27) yields,

\[
(\Delta \phi) (t) = (\Delta \phi) (\infty) \left[1 - e^{-t/\tau_\star}\right] \quad \text{(28)}
\]

where, \( \tau_\star = \frac{1}{R C} \) when boundary condition \( t = 0 \), \( (\Delta \phi) = 0 \) is used. Equation (28) shows the exponential build-up of streaming potential with time.

**Materials and Methods**

Physical characteristics of Zeokarb 225 (Permutit, UK) and Amberlite IRC(50) (Rohm and Haas) are summarized in Table 1. Membranes from these ion exchangers were prepared as described elsewhere. Methanol (BDH, AR) was used as such without further purification.

The experimental set-up used for hydrodynamic permeability and electroosmotic pressure measurements was the same as described earlier. Membrane was equilibrated with the experimental liquid for over 24 hr before use. The experimental solution was
renewed to ensure that its composition remained the same as before the equilibration. A constant known magnitude of pressure difference was imposed by maintaining a constant difference in the level of the liquid on the two sides of the membrane and the ensuing hydrodynamic volumetric flux estimated by following the advancement of the liquid/air meniscus in a horizontally placed graduated capillary tube of predetermined cross-sectional area. For electroosmotic pressure measurements, constant known magnitude of potential difference was applied from an electronically operated stabilized power supply with the help of two coiled platinum electrodes placed in contact with the two faces of the membrane. The corresponding difference of pressure in the vertical liquid columns on the two sides of the membrane was followed as a function of time with the help of a cathetometer reading to 0.001 cm. Time was recorded with a stop watch reading up to 0.1 sec. The cross-sectional area of the electroosmotic pressure measuring capillary was measured by taking the weight of mercury filling a known length in the capillary. Length was measured with the help of a vernier microscope reading up to 0.001 cm.

Streaming potentials developed during the streaming of methanol across different membranes were measured using a Lindemann electrometer. The experimental set-up and procedure followed were the same as described earlier. Methanol was streamed across the membrane under the action of a constant difference in the level of the liquid on the two sides of the membrane. Streaming potential build-up was measured with the help of two coiled platinum electrodes touching the two membrane faces by previously calibrated Lindemann electrometer. The uncertainty in the measured streaming potential was ±1 mV.

All the measurements were carried out in an air-thermostat maintained at 30±0.5°C.

Results and Discussion

Data on build-up of electroosmotic pressure for an Amberlite IRC (50) membrane/methanol system at two values of \( \Delta \phi \) are plotted as a function of time\( (t) \) in Fig. 1. It is evident from Fig. 1 that electroosmotic pressure, \( (\Delta P) \), increases with time and finally attains a steady value. Validity of Eq. (18) has been tested in Fig. 2 wherein \( \log [(\Delta P) \, (00) - (\Delta P) \, (t)] / (\Delta P) \, (00) \) has been plotted against \( t \). All the plots are linear showing the validity of Eq. (18). The values of \( \tau_s \) estimated from the slope of these linear plots are: 0.31 min. at 400 V and 0.29 min. at 500 V.

To test further, the values of \( \tau_s \) obtained in the above manner have been compared with its value calculated from hydrodynamic permeability measurements. The data on hydrodynamic flow of methanol across the membrane included in Fig. 3 clearly show linear dependence on \( \Delta P \), in accordance with Eq. (5). Phenomenological coefficient, \( L_{11}/T \) estimated from the slope of the plot of \( (J)_{\phi=0} / \Delta P \) against \( \Delta P \) is \( 0.60 \times 10^{-3} \) cm\(^2\) sec\(^{-1}\) deg\(^{-1}\). Cross-sectional area of the measuring capillary was \( 1.11 \times 10^{-2} \) cm\(^2\). Using Eq. (19), it is found that,
\[
\tau_e = \frac{1.11 \times 10^{-2}}{0.60 \times 10^{-3}} \times \frac{1}{60} = 0.31 \text{ min.}
\]

This is in very good agreement with the values (0.31 at 400 V and 0.29 at 500 V) obtained from the electro-osmotic pressure data.

As a further internal check on the derived Eqs. (18) and (22), measurements on both build-up and decay of electroosmotic pressure across a different Amberlite IRC (50) membrane/methanol system have been made. The data are included in Fig. 4. Applicability of Eqs. (18) and (22) have been examined in Figs 5 and 6 respectively. The relaxation times for the build-up and decay of electroosmotic pressure, estimated from the slope of these linear plots, are compared in Table 2. The \( \tau_e \) values seem to be in good agreement. Moreover, it should be noted that the observed independence of \( \tau_e \) on \( \Delta \phi \) is in conformity with the requirements of the derived equations since none of the parameters in Eq. (19) is likely to change when \( \Delta \phi \) is varied.

Build-up of streaming potential with time is similar to that of electroosmotic pressure. A typical plot...
for Zeokarb 225 (Na⁺-form)/methanol system is given in Fig. 7. Similar plots are obtained for Ba²⁺ and Al³⁺ forms of the membrane. Validity of Eq. (28) has been examined in Fig. 8 by plotting log \[ \frac{(\Delta \phi)(\infty) - (\Delta \phi)(t)}{(\Delta \phi)(\infty)} \] against \( t \). All the plots are linear as required by Eq. (28). \( \tau_1 \), estimated from the slope of these plots are included in Table 3 for different forms of the ion-exchanger at five different values of streaming pressure. It is evident from Table 3 that \( \tau_1 \) values are practically independent of streaming pressure as expected on the basis of Eq. (29).

It can be seen from Table 3 that \( \tau_1 \) decreases for the different ionic forms of the ion-exchanger membrane in the order, Na⁺ > Ba²⁺ > Al³⁺. It is obvious from Eq. (29) that \( \tau_1 \) is inversely related to equilibrated membrane resistance \( R \) and electrometer capacitance \( C \). With replacement of one counter-ion by another, \( C \) will not change and hence, observed order must be due to changes in \( R \) in different environments. As the self-dissociation of methanol is very small, changes in \( R \) would be due to alterations in the degree of ionization of the ion-exchanger in different environments. The selectivity sequence \( \text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+ \) of cation exchangers, such as Zeokarb 225, for different counterions indicates an opposite trend for the degree of dissociation. Hence, equilibrated membrane resistance would follow the order \( \text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+ \). This explains the decreasing trend of \( \tau_1 \) since, it is directly related to \( 1/R \).

**Acknowledgement**

The authors are highly grateful to Professor R. P. Rastogi, Head, Chemistry Department, for his keen interest, providing necessary facilities and constructive suggestions. Financial assistance rendered by University Grants Commission, India, is also gratefully acknowledged.

**References**