Non-linear Fluxes & Second Order Coefficients

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Factors responsible for the occurrence of second order coefficients in non-linear fluxes have been examined. In this context double layer model for the second order coefficients in streaming current has been postulated which is based on a similar model for the second order coefficient in electroosmotic flux. It is shown that available experimental data support the model.

Experimental investigations in the last decade have shown that fluxes in non-equilibrium situation can be non-linear function of thermodynamic forces. Some of the notable examples are electroosmotic flux\(^1\)\(^-\)\(^3\), streaming current\(^4\)\(^-\)\(^5\) and chemical reaction rate\(^6\). Recent experiments have shown that first order coefficients obey Onsager relation even when the fluxes are non-linear\(^7\).

In this paper, we wish to examine the reasons for the appearance of non-linearity in electrokinetic phenomena and propose a model for the second order coefficients.

Non-linear Fluxes

Non-linearity can arise on account of following factors: (i) Appearance of velocity gradients in the system as can happen during coupling of mass flux and heat flux\(^7\). (ii) Appearance of higher order terms in the expansion of forces as in chemical reactions\(^6\). (iii) Dependence of phenomenological coefficients on intensive properties\(^8\) as in coupling of mass flux and heat flux\(^7\). (iv) Dependence of phenomenological coefficients on the characteristics of the system which depend on forces such as in electroosmosis\(^10\).

So far as the present investigation is concerned factors (i) and (ii) are out of question. It is worthwhile to investigate whether (iii) can explain non-linearity observed in electroosmotic flux in pyrex and quartz membranes using methanol, acetone and ethyl methyl ketone as permeants\(^11\)\(^-\)\(^13\) and ion-exchange membrane/methanol system\(^12\)\(^-\)\(^13\). Ion-exchange membranes are charged membranes whereas the pyrex or quartz\(^3\) membranes are uncharged. The pore size of the channel was much larger than Debye length in the experiments cited above. We will examine the transport equations for such membranes in the following paragraphs:

Capillary model—This is simplest model which has been tried for such systems. The assumptions involved are: (a) The Debye length is very small as compared to the radius of the capillary. This implies that the fluid is electrically neutral over virtually the entire cross-section of the tube. (b) The charge on the wall is so small that the Debye-Hückel linearization of the Poisson-Boltzmann equation is permissible since zeta potential given by the Chapman-Guoy equation is small.

The above model with minor modifications has been developed by Osterele\(^14\), Kobatake and Fujita\(^15\), Gross and Osterele\(^16\) and Mehta and Morse\(^17\).

We shall now examine whether capillary model predicts second order coefficients. We shall consider two cases: (a) when the radius of the capillary is much larger than the Debye length; and (b) when the radius of the capillary is comparable to Debye length.

Case (a)—We shall first consider the capillary model which will hold good in our case. Ion flux \(J_i\) in the \(x\)-direction is given by Nernst-Planck equation\(^16\),

\[
J_i = \bar{C}_i \mu_i - K_i Z_i \bar{C}_i F \left( \frac{\partial \bar{\psi}}{\partial x} \right) - D_i \left( \frac{\partial \bar{C}_i}{\partial x} \right) \quad \ldots (1)
\]

where \(\bar{C}\) designates properties within the tube; \(i = 1\) indicates the cations and \(i = 2\) the anions; \(u\) is the fluid velocity in the \(x\)-direction; \(K_i\) represents the ion mobility; \(D_i\) is the ion diffusivity and \(\bar{C}_i\) the ionic concentration in the tube; \(Z\) denotes the valency of ions; and \(F\) the Faraday constant. The mobility and diffusivity are related by the Einstein relation\(^2\)

\[
K_i = D_i / RT \quad \ldots (2)
\]

where \(R\) is the gas constant. The fluid must obey the Navier-Stokes equation

\[
-\bar{\Delta}p - F \sum_{z=1}^{2} Z_i \bar{C}_i \nabla \bar{\psi} + \eta \nabla^2 u = 0 \quad \ldots (3)
\]

The second term is the electrical body force and \(\bar{\psi}\) is the total pressure. It has been recognized that \(\bar{p} = p_0 + p_1\), where \(p_0\) is applied pressure and \(p_1\) is osmotic pressure. The ionic strength in the tube is given by Boltzmann equation\(^4\)

\[
\bar{C}_i = C \exp( - Z_i F \bar{\psi} / RT) \quad \ldots (4)
\]
where \( \psi \) measures the effect of departure from electroneutrality and \( C \) is a constant. On integrating twice the axial component of Eq. (3) with respect to the radius, we obtain fluid velocity, \( u \), for one component system (i.e. when \( \frac{\partial C}{\partial x} = 0 \)).

\[
u = \frac{a^2 - r^2}{4} \left( -\frac{dp_0}{dx} \right) + \frac{Z_i F}{\eta} \int_{r_1}^{r_2} (C_1 - C_2) dr \left( -\frac{d\phi}{dx} \right) \quad \ldots (5)
\]

where \( a \) is the radius of the capillary and the value of \( r \) varies from 0 to \( a \). In this expression it is supposed that viscosity is constant throughout the tube which would actually be the case if \( r_1 \) and \( r_2 \) are dummy variables of integration.

The volumetric flux, \( J_v \), and current, \( I \), in a capillary tube can be expressed by the relations\(^1\)

\[
J_v = 2\pi \int_0^a ur dr \quad \ldots (6)
\]

\[
I = 2\pi Z F \int_0^a (J_1 - J_2) r dr \quad \ldots (7)
\]

Putting the value of \( u \) from Eq. (5) into Eq. (6), we obtain

\[
J_v = \frac{a^2 A}{8\eta} \left( -\frac{dp_0}{dx} \right) + \left( -\frac{2\varepsilon A}{a^2 \eta} \right) \int_0^a \left( r\psi_a - \psi \right) dr \left( -\frac{d\phi}{dx} \right) \quad \ldots (8)
\]

where \( \varepsilon \) is dielectric constant of the permeant and \( A \) is the cross-section area of the tube. Similarly we can write an expression for \( I \) as follows:

\[
I = \left( -\frac{2\varepsilon A}{a^2 \eta} \right) \int_0^a \left( r\psi_a - \psi \right) dr \left( -\frac{d\phi}{dx} \right) + \left[ \frac{2Z_i^2 F^2 A}{RTa^2} \int_0^a \left\{ K_1 \exp \left( -\frac{Z_i F\psi}{RT} \right) K_2 \exp \left( \frac{Z_i F\psi}{RT} \right) \right\} r dr + \frac{2\varepsilon A}{a^2 \eta} \int_0^a \left( \frac{\partial C}{\partial r} \right)^2 dr \right] \left( -\frac{d\phi}{dx} \right) \quad \ldots (9)
\]

In this expression \( \psi \) is of course, related to \( r \) by Poisson-Boltzmann equation, when the mobilities of cations and anions are assumed to be the same. Equations (8) and (9) can be further simplified\(^1\) since

\[
\cosh \left( Z_i F\psi \right. \frac{RT}{1} = 1
\]

\[
\int_0^a (r\psi_a - \psi_a) dr = 0
\]

and

\[
\int_0^a (r\psi_a - \psi) dr = \frac{1}{2} a^2 \psi_a
\]

Accordingly Eqs (8) and (9) reduce to

\[
J_v = \frac{a^2 A}{8\eta} \left( -\frac{dp_0}{dx} \right) + \left( -\frac{\varepsilon A \psi_a}{\eta} \right) \left( -\frac{d\phi}{dx} \right) \quad \ldots (11)
\]

\[
I = \left( -\frac{\varepsilon A \psi_a}{\eta} \right) \left( -\frac{d\phi}{dx} \right) + \frac{Z_i^2 F^2 K^2}{D} \left( -\frac{d\phi}{dx} \right) \quad \ldots (12)
\]

Since we are considering pure non-electrolyte solvent as a permeant, the ionic concentration in the pore will be extremely low. Therefore, \( \varepsilon, \psi_a \) and \( \eta \) may be taken to be constant throughout the pore. Thus on integration of Eqs (11) and (12) across the membrane, we would get equations where \( dp_0/dx \) and \( d\phi/dx \) are simply replaced by \( \Delta P/1 \) and \( \Delta \phi/1 \).

Case (b)—When the pore size of the channel is comparable to Debye length, the transport equations would be different. The Nernst-Planck equation for cations and anions in a cell would be written as\(^17\)

\[
J_1 = -D_1 \frac{dC_1}{dx} \frac{\partial C_1}{\partial x} Z_1 F \frac{\partial \phi}{\partial x} \quad \ldots (13)
\]

\[
J_2 = -D_2 \frac{dC_2}{dx} \frac{\partial C_2}{\partial x} Z_2 F \frac{\partial \phi}{\partial x} \quad \ldots (14)
\]

For one-component system, \( \frac{\partial C_1}{\partial x} = 0; \frac{\partial C_2}{\partial x} = 0 \)

and \( Z_1 = Z_2 = Z \)

The current flux is defined as

\[
I = J_1 - J_2 F Z \quad \ldots (15)
\]

Putting the values of \( J_1 \) and \( J_2 \) from Eqs (13) and (14) into Eq. (16) we obtain

\[
I = (C_1 D_1 + C_2 D_2) \left( \frac{Z_i^2 F^2}{RT} \right) \left( -\frac{\partial \phi}{\partial x} \right) + F Z (C_1 - C_2) \quad \ldots (17)
\]

Fluid velocity, \( u \), in terms of applied gradient is given by

\[
u = d_a \left[ -F Z (C_1 - C_2) \frac{d\phi}{dx} \frac{dp_0}{dx} \right] \quad \ldots (18)
\]

where \( d_a \) is a measure of the mechanical permeability of the membrane, the so-called 'hydrodynamic permeability' and \( F Z (C_1 - C_2) \) is the electrical space charge in a unit volume of the cell. The flux, \( J_v \), due to applied pressure difference and potential difference is written as

\[
J_v = \frac{B_0}{\eta} \left( -\frac{dp_0}{dx} \right) + \frac{B_0}{\eta} F Z (C_1 - C_2) \left( -\frac{d\phi}{dx} \right) \quad \ldots (19)
\]

where \( B_0 \) is permeability coefficient and is given by

\[
B_0 = \frac{a^4}{4} \frac{(1 - \gamma^3)}{18} \frac{1}{\gamma + 1} (1 - \gamma)^{-5} \quad \ldots (20)
\]

where \( \gamma = a/b; a \) and \( b \) are the radii of concentric spheres. Putting the value of \( u \) from Eq. (18) into Eq. (17) we obtain
\[ I = FZ(\bar{C}_1 - \bar{C}_2)d_h \left( -\frac{d\varphi}{dx} \right) \]

\[ + \frac{Z^2 F^2}{RT}(\bar{C}_1 D_1 + \bar{C}_2 D_2) + RT(\bar{C}_1 - \bar{C}_2)^2 d_h \left( -\frac{d\varphi}{dx} \right) \]

... (21)

Equations (19) and (21) can be written in terms of phenomenological coefficients as follows:

\[ J_v = L_{11}\left( -\frac{d\varphi}{dx} \right) + L_{12}\left( \frac{d\varphi}{dx} \right) \]  

... (22)

\[ I = L_{21}\left( -\frac{d\varphi}{dx} \right) + L_{22}\left( \frac{d\varphi}{dx} \right) \]  

... (23)

where \( L_{11} = \frac{B}{\eta} = d_h \)

\[ L_{12} = L_{21} = FZ(\bar{C}_1 - \bar{C}_2)d_h \]  

... (24)

and \( L_{22} = \frac{Z^2 F^2}{RT}(\bar{C}_1 D_1 + \bar{C}_2 D_2) + RT(\bar{C}_1 - \bar{C}_2)^2 d_h \)

Here again, all the terms appearing in the phenomenological coefficients would be constant for the systems under reference and hence the integration across the membrane will not yield non-linear terms.

Thus, the capillary model does not predict second order coefficients and hence we have to look for an alternative model. It has to be noted that electrokinetic phenomena are different from diffusion phenomena in view of the fact that membrane structure and the structure of the double layer has to be taken into account. This is corroborated by strong experimental evidence as follows:

(a) In case of ion-exchange membrane, both electroosmotic flux as well as electrophoretic velocity have been found to be non-linear in \( \Delta \varphi \), where even the change of direction of the flux can occur on increasing \( \Delta \varphi \). The experimental results are mutually consistent since the sign of inversion occurs at a particular value of \( \Delta \varphi \) for both electroosmotic flux and electrophoretic velocity. Non-linearity in electrophoretic velocity cannot be ascribed to the effect of mathematical integration across the membrane since in the case of electrophoretic velocity no membrane is involved.

(b) Non-linearity is observed in the case of electroosmosis of non-aqueous permeants only and not in the case of aqueous solutions of electrolytes. Sign inversion is obtained in case of weak cation-exchanger membrane and not for strong ion-exchange membranes. This only suggests that physical factors have to be searched in order to account for non-linearity in electro-kinetic phenomena.

**Model for Second Order Coefficients**

Experimental results show that electroosmotic flux \( (J)_{\Delta \varphi = 0} \) and streaming current, \( (I)_{\Delta \varphi = 0} \) are given by


\[ (J)_{\Delta \varphi = 0} = L_{12}\left( \frac{\Delta \varphi}{T} \right) + \frac{1}{2} L_{122}\left( \frac{\Delta \varphi}{T} \right)^2 \]  

... (25)

\[ (I)_{\Delta \varphi = 0} = L_{21}\left( \frac{\Delta \varphi}{T} \right) + \frac{1}{2} L_{211}\left( \frac{\Delta \varphi}{T} \right)^2 \]  

... (26)

where \( L_{112} \) and \( L_{21} \) are first order phenomenological coefficients and \( L_{122} \) and \( L_{211} \) are the second order phenomenological coefficients. Electrokinetic theory based on electrical double layer shows that \( L_{112} \) and \( L_{21} \) are related to zeta-potential. However, this theory as such cannot explain the origin of \( L_{122} \) and \( L_{211} \). Intuitively one would imagine it to depend on the properties of double layer, i.e. the influence of electric field and the pressure difference on double layer character. A model for explaining the origin of \( L_{122} \) has been suggested using modified picture of electrical double layer as shown in Fig. 1 which shows that the effective zeta-potential, \( \xi_{\text{eff}} \), will be made up of \( \Delta \varphi \), the charge contribution potential and dipolar potential, \( \Delta \chi \), so that

\[ \xi_{\text{eff}} = \Delta \varphi + \Delta \chi \]  

... (27)

Dipolar potential difference would depend on applied field strength \( \bar{X} \) as follows:

\[ \Delta \chi = \frac{\mu N_T \mu \cdot \bar{X}(1 - C)}{4 \pi \varepsilon r_0} \]  

... (28)

where \( \mu \) is dipole moment, \( C \) is the number of dipoles which interact with a particular dipole, \( N_T \) is the total number of dipoles adsorbed on the interface. \( r_0 \) is the magnitude of radius vector.

Inserting the value of \( \Delta \chi \) from Eq. (28) into Eq. (27) we obtain

\[ \xi_{\text{eff}} = \Delta \varphi + \frac{N_T \mu \cdot \bar{X}(1 - C)}{4 \pi \varepsilon r_0} \]  

... (29)

![Figure 1: Schematic representation of the structure of electrical double layer](image-url)
Thus, it is seen that the resultant field in the double layer will be due to charges in the double layer and dipoles adsorbed at the interface.

The electroosmotic flux, \( J_{(\psi)} \), through a capillary of radius \( a \) and length \( l \) is given by

\[
J_{(\psi)} = \frac{a^2 \varepsilon \mathbf{X} \mathbf{X}}{4\pi}  
\]

Substituting the value of \( \xi_{\text{eff}} \) from Eq. (29) into Eq. (30) we obtain

\[
J_{(\psi)} = \frac{a^2 \varepsilon \mathbf{X} \mathbf{X}}{4\pi} \mathbf{X} \mathbf{X} \left[ \frac{a^2 N_{TF}(1-C)\mu^*}{16\pi \eta^2 K} \mathbf{X} \mathbf{X} \right] \left( \mathbf{X} \mathbf{X} \right) \]...

On comparing Eq. (31) with Eq. (25), we obtain

\[
L_{12} = \frac{a^2 \varepsilon}{4\eta^2} \Delta \phi \]

and

\[
L_{12} = \frac{a^2 N_{TF}(1-C)\mu^*}{8\pi \eta^2 K} \frac{1}{\mathbf{X} \mathbf{X}} \]

Since \( \mathbf{X} = \Delta \phi / \mathbf{X} \), Eq. (33) justifies the vectorial character of \( L_{12} \). Although, we have taken the case of water dipoles as an illustration, the above treatment is perfectly general. Equation (33) shows that \( L_{12}/T \) depends on (i) \( N_{TF} \), the total number of adsorbed dipoles, (ii) \( \eta \), viscosity of the medium and (iii) \( \mu^* \), dipole moment vector.

\( N_{TF} \) and \( \mu^* \) would depend on the nature of electrical double layer which in turn would depend on the nature of the permeant and the membrane. Accordingly, it is possible to alter the double layer in such a way that \( L_{12}/T \) has a negative sign and a change in the direction of electroosmotic flow may occur. The condition for the reversal in direction is given by

\[
\Delta \mathbf{P} \mathbf{X} \mathbf{X} \mathbf{X} \mathbf{X} > L_{12} \]

Such changes in double layer structure will be more pronounced when the membrane is composed of weak ion-exchange material because then the charge density would be very small due to incomplete dissociation of fixed ionic group. In the case of strong ion-exchange membrane, the dissociation of the fixed ionic group (such as \(-\text{SO}_3\mathbf{H}\)) is almost complete even in non-aqueous solvent. Thus, the theory predicts that (i) sign reversal in electroosmotic flux can occur when a membrane composed of weak ion-exchange material is used and (ii) when a membrane composed of a strong ion-exchange material is used, no change in the direction of electroosmosis is expected. These predictions are found to be in accord with experimental observations.

The purpose of this section is to examine a similar type of model for explaining non-linearity in streaming current, i.e. the origin of the second order coefficient \( L_{211} \) in Eq. (26).

When pressure difference is applied, the double layer formed at the interface will undergo strain. The magnitude of the strain will depend on the stress, i.e. the applied pressure difference. It is easy to visualize how this would happen with the help of Fig. 2. Let us suppose that the thickness of the double layer before the application of stress is \( d_0 \). However, if a stress is applied, the outer Helmholtz plane (OHP) would be pushed by an angle \( \theta \), so that the effective thickness of the double layer would be \( d_0 \cos \theta \). The lateral strain would be equal to \( (d_0 - d_0 \cos \theta) / d_0 \). The corresponding longitudinal strain would be \( (d_0 - d_0 \cos \theta) / d_0 \), where \( \sigma' \) is called Poisson's ratio. It has to be noted that the stress would be \( \Delta \mathbf{P} \). Thus, the modulus of rigidity, \( \chi \), of the double layer would be given by

\[
\chi = \Delta \mathbf{P} \sigma' / (d_0 - d_0 \cos \theta) \]

where, \( \mathbf{i} \) is unit vector. On rearranging, we get

\[
\Delta \mathbf{P} \sigma' = \chi (d_0 - d_0 \cos \theta) \]

i.e.

\[
x = \chi \sigma' / (1 - \cos \theta) \]

Now, the charge contribution potential \( \Delta \psi_{\text{eff}} \) would be given by

\[
\Delta \psi_{\text{eff}} = \frac{4\pi e d_0 \cos \theta}{a} \]

where, \( e \) is the charge density. Putting the value of \( \cos \theta \) from Eq. (36) into Eq. (37), we get

\[
\Delta \psi_{\text{eff}} = \Delta \psi_0 \left( 1 - \frac{\Delta \mathbf{P} \sigma'}{\chi} \right) \]

where \( \Delta \psi_0 \) is equal to \( 4\pi e d_0 a \). Thus, the effective zeta-potential would be given by

\[
\zeta_{\text{eff}} = \Delta \psi_0 \left( 1 - \frac{\Delta \mathbf{P} \sigma'}{\chi} \right) \]
Further, the streaming current, \( I_{\Delta \Psi} \), across a capillary channel of radius \( a \) and length \( l \) would be given by:\(^{18}\)

\[ I_{\Delta \Psi} = \frac{a^2 \varepsilon \sigma \Delta \Psi_0}{4\eta l} \Delta \Psi \quad \text{... (40)} \]

Putting the value of \( \xi_{\text{eff}} \) from Eq. (39) into Eq. (40), we obtain

\[ I_{\Delta \Psi} = \frac{a^2 \varepsilon \xi_{\text{eff}} \Delta \Psi_0}{4\eta l} \Delta \Psi \quad \text{... (41)} \]

On comparing Eq. (41) with Eq. (26) we get

\[ L_{21}, \tau = \frac{a^2 \varepsilon \Delta \Psi_0}{4\eta l} \quad \text{... (42)} \]

and

\[ \frac{1}{2} \left( \frac{L_{211}}{L_{21}} \right)^2 = \frac{a^2 \varepsilon \Delta \Psi_0 \sigma'}{4\eta l^2} \quad \text{... (43)} \]

On combining Eqs (42) and (43) we get

\[ \frac{1}{2} \left( \frac{L_{211}}{L_{21}} \right)^2 = \frac{-\sigma'}{i_z} \quad \text{... (44)} \]

Equation (44) shows that the direction of the vector \( L_{211} \) would depend on the direction of the unit vector \( i_z \). The latter would be determined by the direction of adsorbed dipoles on the membrane interface, and accordingly \( L_{211} \) can have both positive and negative sign. We note that according to Eq. (44), the term \( L_{211} \) depends on two important parameters associated with the double layer, viz. Poisson's ratio and modulus of rigidity which are difficult to estimate theoretically or to determine experimentally. Hence, it is not easy to check the validity of the model. Nevertheless, the structure of the diffuse double layer and the nature of the ions in the diffuse double layer can give a relative idea of the Poisson's ratio and modulus of rigidity. Thus, relative magnitude of \( L_{211} \) for different types of double layers can be predicted.

We will examine the validity of the model in terms of the available data.\(^3\) From the data, we find that for water \( i \) would be positive corresponding to the direction of flip up dipoles (\( + \)) while for methanol \( i \) would be negative corresponding to the direction of flip down dipoles (\( - \)). Thus, \( (L_{211} \tau^2)(L_{21} \tau) \) for \( \text{H}_2\text{O} \) would be positive while that for methanol the quantity would be negative. This prediction is supported by the experimental data\(^3\) which shows that

\[ \left[ \frac{L_{211} \tau^2}{L_{21} \tau} \right]_{\text{H}_2\text{O}} = 0.13 \times 10^{-4} \text{ dynes}^{-1} \text{ cm}^2 \]

and

\[ \left[ \frac{L_{211} \tau^2}{L_{21} \tau} \right]_{\text{H}_2\text{O}} = -0.19 \times 10^4 \text{ dynes}^{-1} \text{ cm}^2 \]

This is understandable since

\[ \left( \frac{\sigma'}{\tau} \right)_{\text{H}_2\text{O}} < \left( \frac{\sigma'}{\tau} \right)_{\text{H}_2\text{OH}} \]

on account of the following reason. Water is more polar than methanol; the double layer formed at membrane-water interface will be more compact than membrane-methanol interface and hence when stress is applied, \( \theta \) would be smaller in the former case so that \( \Delta \Psi_{\text{eff}} \) would be more (Eq. 37) in the case of membrane-water system. Consequently the above inequality would be justified. Further, it follows from the above model that

\[ \sigma' = (1 - \cos \theta) \sigma \]

Lower value of \( \theta \) means lower values of \( \sigma' \) which justifies the above inequality.

Thus the predictions of the above model are in qualitative agreement with available experimental observation.

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References