EXPERIMENTAL ACCESIBILITY OF SINGLE-ION ACTIVITY COEFFICIENTS

IN THE CHARGE-CONTROLLED TIME DOMAIN

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Summary .-

Irreversible Thermodynamics is applied to binary electrolyte solutions to study the charge separation process ocurring in a free-diffusion liquid junction. Transport equations and Poisson equation are solved by using Fourier cosine series. A comparison with equivalent results obtained by numerical solution of Nernst-Planck/Poisson equations is made. An electrical analogy between the charge separation process and the charging process of a capacitor is established. The results obtained for the full cell potential are used to discuss the experimental accesibility of single-ion coefficients.

1.- Introduction .-

In a recent paper (Mafé et al.,1988), Nernst-Planck flux equations and Poisson equation were used to provide a detailed description of the charge separation process in non-homogeneous electrolyte solutions. The relevance of the "diffusional" and "electric" relaxations were analysed. The classical treatment by Planck was shown to be equivalent to ignoring the whole charge separation process.

In this paper we extend the above analysis by solving the Non-equilibrium Thermodynamics equations and introducing single-ion activity coefficients in our treatment. The Onsager reciprocal relations are assumed throughout. The transport equations are expressed in terms of the ionic strength and the electric charge density. The resulting equations are assumed to be linear in order to be solved.

Our aim is to obtain expressions for the full cell potential which allow us to discuss the experimental accesibility of a single-ion activity coefficients.

2.- Applicability of a classical treatment

Previous studies of the charge separation process (Jackson 1974; Leckey and Horne 1981; Mafé et al., 1988) involve times of the order of the electric relaxation one,

τ_e - 10^{-9} s, and distances of the order of the Debye length of the problem, L_D-10^{-7}cm (that is, close to the limit of validity of this macroscopic theory).

So far the studies on this problem are based on classical ideas, but it is also known that certain aspects of the interfacial electrochemistry (Bockris and Reddy 1978) requires quantum treatment. Thus it is interesting to consider the validity of a classical study as a previous step to the resolution of the phenomenological equations.

As we have just mentioned, the charge separation process begins over spatial regions of L_D- 10 Å. The wavelength of de Broglie can be evaluated associating a thermal kinetic energy to the ions

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_c}} \approx \frac{hN_A}{\sqrt{3MRT}} \qquad /1/$$

being k Boltzmann's constant, N_A Avogadro's number, R the gas constant, T the absolute temperature, h Planck's constant and M the molecular weight.

For the sodium ion e.g., we indeed obtain a value for the wavelength of de Broglie much lower than that of the Debye length:

$$\lambda \sim 10^{-1} \overset{\circ}{A} \ll 10 - 10^2 \overset{\circ}{A} \sim L_D = \sqrt{\varepsilon RT/F^2 c_0}$$

/2/

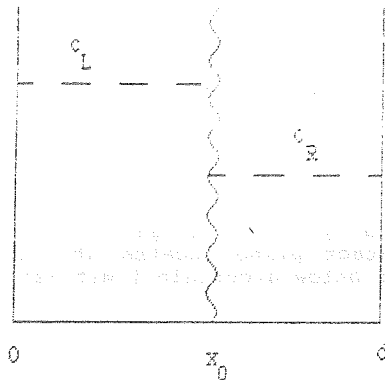where c_0 is a scale concentration. Then the classical treatment seems to be right.

Figure 1

1. $d \gg L_D$ 2. $\dfrac{|c_L - c_R|}{c_R} \ll 1$ 3. $x_0 \approx \dfrac{d}{2}$, $t = 0$

Schematic representation of the transport problem considered. At t=0, two solutions of the same binary electrolyte at diferent concentrations ($c_{L,R}$) are brought into contact at a central point (3). The difference in their concentrations is small compared with their absolute values (2). As usual, the diffusion zone thickness is much greater than the Debye length of the problem (1).

3.- Nerst-Planck flux equation description.-

The situation analysed is shown in detail in Figure 1. Two solutions of the same binary electrolyte at different concentrations are brought into contact at a mid-point $x = x_0$ (instant t=0). The magnitudes of ionic concentrations are assumed to be small enough so that the transport equations can be approximated by Nerst-Planck flux equations (Buck 1.984). Solvent flow is assumed to be negligible and there are no externally applied electric fields. Ionic diffusion coefficients and dielectric constant are considered to be constant along the diffusion zone.

As the walls of the cell are impenetrable, the boundary conditions can be expressed in the following way:

$$J_i(0, t) = J_i(d, t); \quad i = 1, 2$$

$$\Phi(0,t)=0, \quad \frac{\partial \Phi}{\partial x}(0,t) = 0, \quad \frac{\partial \Phi}{\partial x}(d,t)=0,$$

/3/

$$\frac{\partial c_i}{\partial x}(0,t) = \frac{\partial c_i}{\partial x}(d,t) = 0; \quad i = 1,2$$

and the initial conditions are

$$c_i(x,0)= \begin{cases} c_L = c_0 + \delta c_0/2 & 0 < x < x_0 \\ \\ c_R = c_0 - \delta c_0/2 & x_0 < x < d \end{cases} \quad (\delta c_0 \ll c_0); \; i=1,2$$

/4/

We reproduce below some results of our previous work (Mafé et al., 1988) relevant to the present analysis. The ionic concentrations are given by

$$c_i(x,t) = c_0 + \frac{2}{\pi}(c_L - c_R) \cdot$$

$$\sum_{m=1}^{N} \frac{\text{sen}\left(\frac{m\pi x_0}{d}\right) \cos\left(\frac{m\pi x}{d}\right)}{m} e^{-m^2 t/\tau_d} \cdot$$

/5/

$$\left[1 + \frac{(-1)^{i-1}}{2\,\alpha_m} \frac{D_1 - D_2}{D_1 + D_2}\left(e^{-t/\tau_e} - 1\right)\right]$$

where the series has been truncated at a given term $N(N < E[d/\pi L_D]$ at the most), owing to $\alpha_m (d/m\pi L_D)^2 \gg 1$. (Here $E[x]$ denotes the integer part of x). τ_e and τ_d appearing in /5/ are, respectively, the electric and the diffusional relaxation times. These are given by

$$\tau_d = \frac{2d^2}{\pi^2(D_1 + D_2)}; \quad \tau_e = \frac{\varepsilon RT}{F^2(D_1 + D_2)c_0}$$

/6/

From equation /5/ is turns out that the electric charge density may be written as

$$\rho(x,t) = F(C_1 - C_2) = \frac{2\pi\varepsilon RT}{Fd^2} \frac{c_L - c_R}{c_0} \frac{D_1 - D_2}{D_1 + D_2} \cdot$$

$$\cdot \left(\sum_{m=1}^{N} m \, \text{sen}\left(\frac{m\pi}{2}\right) \cos\left(\frac{m\pi x}{d}\right) e^{-m^2 t 7\tau_d} \right) \left(e^{-t/\tau_e} - 1 \right)$$

/7/

where we have taken $x_0 = d/2$.

The electric potential difference arising between the two electrolyte solutions (namely, the liquid juntion potential) is

$$\Phi_{U.L.} = \Phi(d,t) - \Phi(0,t) = \frac{4}{\pi} \frac{RT}{F} \frac{D_1 - D_2}{D_1 + D_2} \frac{c_L - c_R}{c_0} \cdot$$

$$\left(\sum_{m=1}^{N} \frac{\text{sen}\left(\frac{m\pi x_0}{d}\right) \text{sen}^2\left(\frac{m\pi}{2}\right)}{m} e^{-m^2 t/\tau_d} \right) \cdot$$

$$\cdot \left(1 - e^{-t/\tau_e} \right) . \qquad\qquad /8/$$

Taking $x_0 \approx d/2$ and writing equation /7/ for the time interval where the charge separation process takes place, $0 < t - \tau_e \ll \tau_d$, we have:

$$\Phi_{U.L.} \approx \frac{RT}{F} \frac{D_1 - D_2}{D_1 + D_2} \frac{\delta c_0}{c_0} \cdot$$

/9/

$$\left(1 - e^{-t/\tau_e} \right) \approx \Delta\Phi_p \left(1 - e^{-t/\tau_e} \right), \quad 0 < t - \tau_e$$

being $\Delta\Phi_p$ the liquid junction potential obtained by Planck (with the local electroneutrality assumption) for the steady state.

It is evident that conduction electric current density, I_q, has a non-zero value in the charge separation process studied here, at least locally and during the "charged-controlled" time domain. Ionic fluxes can be calculated from Nernst-Planck

equation simply by sustituting $c_i(x,t)$ and $\partial\phi/\partial x$ in it. Then, at the contact point $x = d/2$, one obtains for I_q.

$$I_q(d/2,t) = F(J_1 - J_2) = I_0 \left(\sum_{k=0}^{N/2} e^{-(2k+1)^2 t/\tau_d} \right) \cdot$$

$$\cdot e^{-t/\tau_e} \qquad\qquad /10/$$

where

$$I_0 = -2F \frac{(D_1 - D_2)(c_L - c_R)}{d} \qquad /11/$$

Finally, the charge carried through the contact plane located at $x = d/2$ can be estimated below a certain limit as:

$$Q_t = \int_0^t I_q(d/2,t)\,dt \approx N' I_0 (-\tau_e) \left(e^{-t/\tau_e} - 1 \right) =$$

$$= Q_0 \left(1 - e^{-t/\tau_e} \right) \qquad /12/$$

4.- Electrical analogy.-

There is a straightforward analogy between the charge separation process and the transient of an RC circuit in direct current. Such analogy is quite useful, since the charge separation process has a difficult interpretation, whilst the behaviour of an RC circuit is much more intuitive. Besides, we are able to design equivalent circuits and reinterpretate the results in terms of the charge separation process considered.

In our process ions move due to concentration gradients, so the fem must be directly proportional to $(c_L - c_R)$. In order to have a magnitude with fem dimensions we can take:

$$\varepsilon = 2 \frac{RT}{F} \frac{c_L - c_R}{c_0} \qquad /13/$$

Capacitance by area unit of a plane paralell capacitor is defined as the

dielectric constant of the medium filling the capacitor over the distance between planes. Let us take:

$$C = \frac{\varepsilon}{L_D} = \frac{Fc_0 L_D}{RT} \qquad /14/$$

We can determine an expression for the resistance by looking for an ohmic term in the expresion for the electric current density. So we find

$$R = \frac{RTL_D}{F^2 D_0 c_0} \qquad /15/$$

which has dimensions of resistance times area unit.

Now, the electric time constant is equal to the electric relaxation time:

$$RC = \frac{L_D^2}{D_0} = \tau_e , \qquad /16/$$

the initial current is

$$I_O = \frac{\varepsilon}{R} = 2 D_0 \frac{c_L - c_R}{L_D} F \qquad /17/$$

and the charge transport at time t is

$$Q = \varepsilon C \left(1 - 2^{-\tau/RC}\right) = Q_O \left(1 - e^{-t/\tau_e}\right) =$$

$$= 2FD_0 \frac{c_L - c_R}{L_D} \tau_e \left(1 - e^{-t/\tau_e}\right). \qquad /18/$$

which agree with previous results.

5.- Irreversible Thermodynamics description.

From a rigorously Thermodynamic point of view, classical reasons justifying experimental inaccesibility of single-ion activity coefficients have been given (Guggenheim 1929; Helfferich 1962). However, the interest of those coefficients has not diminished (Goldberg and Franck 1972; Leckey and Horne 1981). The problem of their accesibility reduces to that posed by the imposibility of the exact evaluation, by thermodynamic methods, of liquid junction potentials (MacInnes 1939). It has long been recognized that if liquid junction potential could be unambigously evaluated, we would be able to obtain single-ion activity coefficients (with additional data from readily accesible electrochemical cells).

Our aim here is to solve Onsager flux equations and Poisson equation to calculate the liquid junction potential for the simplest possible case, a free-diffusion liquid junction of the same binary electrolyte. Then it would be possible to use this information to determine the feasibility of measurements of sigfle-ion activity coefficients.

Following Franck (1963) we consider the mean ionic activity coefficient $\gamma = \sqrt{\gamma_1 \gamma_2}$, and the mean ionic activity deviation, $\delta = \sqrt{\gamma_1/\gamma_2}$, being γ_1 and γ_2 the single-ion activity coefficients of cation and anion, respectively. To perform the calculations, it is convenient to introduce other two related parameters:

$$B = \frac{\ln \delta}{I} \; ; \qquad M = \left(\frac{\partial \ln \gamma}{\partial I}\right)_{T,P} .$$

$$/19/$$

being $I = (c_1 + c_2)/2$ the ionic strength.

Time variation of ionic concentrations is given by the continuity equations and the Onsager phenomenological equations:

$$- J_i = \sum_{j=1}^{2} l_{ij} \left(\frac{\partial \tilde{\mu}_j}{\partial x}\right) ; \; i = 1,2 \quad /20/$$

where the l_{ij}'s are the Onsager transport coefficients.

The values of the electrochemical potential gradients can be expressed in the form:

$$\frac{\partial \tilde{\mu}_1}{\partial x} = \frac{RT}{c_1} \frac{\partial c_1}{\partial x} + RT (M + B) \frac{\partial I}{\partial x} + F \frac{\partial \phi}{\partial x}$$

$$/21/$$

$$\frac{\partial \tilde{\mu}_2}{\partial x} = \frac{RT}{c_2} \frac{\partial c_2}{\partial x} + RT(M - B) \frac{\partial I}{\partial x} - F \frac{\partial \Phi}{\partial x}$$

Now, ionic fluxes can be calculated from equation /20/ as:

$$-J_i = \beta_i \frac{\partial \Phi}{\partial x} + \sum_{j=1}^{2} \alpha_{ij} \frac{\partial c_j}{\partial x} \qquad /22/$$

being

$$\alpha_{ij} = RT \left[\frac{l_{ij}}{c_j} + \frac{l_{ii}}{2}(M + z_i B) + \frac{l_{12}}{2}(M - z_i B) \right] \qquad /23/$$

$$\beta_i = F(l_{11} - l_{12})$$

As we are concerned with a free-diffusion junction and the cell is free of electric charge, the boundary conditions are

$$J_i(0,t) = J_i(d,t) = 0; \quad i = 1,2 \qquad /3/$$

$$\Phi(0,t) = 0, \quad \frac{\partial \Phi}{\partial x}(0,t) = 0, \quad \frac{\partial \Phi}{\partial x}(d,t) = 0$$

$$\frac{\partial c_i}{\partial x}(0,t) = \frac{\partial c_i}{\partial x}(d,t) = 0; \quad i = 1,2 .$$

On the other hand, initial conditions are

$$c_i(x,0) = \begin{cases} c_L = c_0 + \delta c_0/2 & 0 < x < x_0 \\ & (\delta c_0 \ll c_0); i=1,2 \\ c_R = c_0 - \delta c_0/2 & x_0 < x < d \end{cases} \qquad /4/$$

being $c_0 = (c_L + c_R)/2$ and $\delta c_0 = c_L - c_R$.

Introducing Poisson equation and expressions for the fluxes into continuity equations

$$\frac{\partial c_i}{\partial t} = - \frac{\partial J_i}{\partial x} \qquad /23/$$

and referring the resulting equations to the magnitudes

$$I = \frac{c_1 + c_2}{2} ; \qquad \rho = F(c_1 - c_2) \qquad /24/$$

we obtain

$$\frac{\partial I}{\partial t} = a_{II} \frac{\partial^2 I}{\partial x^2} - a_{I\rho} \frac{\partial^2 \rho}{\partial x^2} + b_I \rho \qquad /25/$$

$$\frac{\partial \rho}{\partial t} = -a_{\rho I} \frac{\partial^2 I}{\partial x^2} + a_{\rho\rho} \frac{\partial^2 \rho}{\partial x^2} - b_\rho \rho$$

where

$$a_{II} = \frac{RT}{2} \left[\frac{l_{11} + l_{12}}{c_1} + \frac{l_{12} + l_{22}}{c_2} + \right.$$
$$\left. + (l_{11} + l_{12})(M + B) + (l_{12} + l_{22})(M - B) \right]$$

$$a_{I\rho} = \frac{RT}{4F} \left[- \frac{l_{11} + l_{12}}{c_1} + \frac{l_{12} + l_{22}}{c_2} \right]$$

$$a_{\rho I} = -RT \left[\frac{l_{11} - l_{12}}{c_1} + \frac{l_{12} - l_{22}}{c_2} + \right.$$
$$\left. + (l_{11} - l_{12})(M + B) + (l_{12} - l_{22})(M - B) \right] \qquad /26/$$

$$a_{\rho\rho} = \frac{RT}{2} \left[\frac{l_{11} - l_{12}}{c_1} - \frac{l_{12} - l_{22}}{c_2} \right]$$

$$b_I = - \frac{F}{2\varepsilon} (l_{11} - l_{22})$$

$$b_\rho = \frac{F^2}{\varepsilon} (l_{11} + l_{22} - 2 l_{12}) .$$

Fourier cosine expansion for I and ρ

$$I = \sum_{m=1}^{\infty} i_m(t) \cos\left(\frac{m\pi x}{d}\right) + c_0 ; \qquad /27/$$

$$\rho = \sum_{m=1}^{\infty} \rho_m(t) \cos\left(\frac{m\pi x}{d}\right)$$

transforms equations /25/ into a system of two coupled ordinary differential equations which can be solved easily by assuming constant coefficients. So, we get

$$I = c_0 + \frac{c_L - c_R}{\pi} \sum_{\substack{k=1 \\ m=2k-1}}^{\infty} \frac{(-1)^{k+1}}{m \; Q_m} \; \cdot$$

$$\cdot \left(P_{+m} \; e^{-t/\tau_m^+} + P_{-m} \; e^{-t/\tau_m^-} \right) \cos\left(\frac{m\pi x}{d} \right) \tag{28}$$

$$\rho = - \frac{2 \, a_{\rho I} \, \pi (c_L - c_R)}{d^2} \sum_{\substack{k=1 \\ m=2k-1}}^{\infty} \frac{(-1)^{k+1} \, m}{Q_m} \cdot$$

$$\cdot \left(e^{-t/\tau_m^+} - e^{-t/\tau_m^-} \right) \cos\left(\frac{m\pi x}{d} \right)$$

being

$$P_{\pm m} = \pm 2 \left(\sigma_m - 1/t_m^{\pm} \right)$$

$$\sigma_m = \gamma_{DD} \, \beta_m + \gamma_D \tag{29}$$

$$\frac{1}{t_m^{\pm}} = - \frac{1}{2} \left[-b_\rho - \left(a_{\rho\rho} + a_{II} \right) \left(\frac{m\pi}{d} \right)^2 \pm Q_m \right]$$

$$Q_m^2 = \left[(a_{\rho\rho} - a_{II})^2 + 4a_{I\rho} a_{\rho I} \right] \left(\frac{m\pi}{d} \right)^4 +$$

$$+ \left[2b_\rho (a_{\rho\rho} - a_{II}) + 4b_I a_{\rho I} \right] \left(\frac{m\pi}{d} \right)^2 + b_\rho^2$$

An analysis of order of magnitudes for expressions /29/ leads to

$$Q_m \sim b_\rho \tag{30}$$

$$\frac{1}{\tau_m^+} \sim \frac{m^2}{\tau_d} \; ; \quad \frac{1}{\tau_m^-} \sim \frac{m^2}{\tau_d} + \frac{1}{\tau_e}$$

Now we are able to get an expression for the liquid junction potential by integrating twice the electric charge density

$$\Phi_{U.L.} \sim \frac{4 \, a_{\rho I}(c_L - c_R)}{\pi \, \varepsilon \, b_\rho} \sum_{k=1}^{\infty} \cdot \tag{31}$$

$$\cdot \frac{(-1)^k}{m} \; e^{-m^2 \tau/t_d} \left(1 - e^{-\tau/t_e} \right)$$

which reduces to equation /8/ in the ideal solutions limit (with $x_0 = d/2$).

Full cell potential can be obtained by adding electrodes contribution, Φ_e, to liquid junction potential:

$$\Phi_C = \Phi_e + \Phi_{U.L.} = - \frac{RT}{F} \left\{ \ln\left(\frac{c_{2R}}{c_{2L}} \right) + \right.$$

$$\left. + \ln\left(\frac{\gamma_{2R}}{\gamma_{2L}} \right) \right\} + \Phi_{U.L.} \tag{32}$$

where $c_{2R,L}$ denote anion concentration in the vicinity of the electrodes (but out of the electric double layer) (Levich 1962).

Introducing mean activity coefficients and the parameter B, equation /32/ yields

$$\Phi_C = \frac{4a_{\rho I}(c_L - c_R)}{\pi \, \varepsilon \, b_\rho} \sum_{\substack{k=1 \\ m=2k-1}}^{\infty} \frac{(-1)^k}{m} e^{-m^2 t/\tau_d} \cdot$$

$$\cdot \left(1 - e^{-t/\tau_e} \right) - \frac{RT}{F} \left\{ \ln\left(\frac{I_R \gamma_R}{I_L \gamma_L} \right) - B(I_R - I_L) \right\} \tag{33}$$

It can be shown that full cell potential depends on B onlt for $t < \tau_e$. In this time interval, we can asssume the linear approximation for $\exp(-t/\tau_e)$ and equation /33/ takes the simpler form

$$\Phi_c \approx - \frac{\rho I \frac{a}{\varepsilon}(c_L - c_R)}{} t - \frac{RT}{F}\left\{\ln\left(\frac{c_R \gamma_R}{c_L \gamma_L}\right) - \right.$$

$$\left. - B(c_R - c_L)\right\} \qquad /34/$$

The above result leads to a possible way of obtaining ionic effects measurements from the full cell potential, although this requires that measurements must be carried out within the electric relaxation process.

Let us consider the system $LiCl-H_2O$ under the following conditions:

$$c_L = 1.1 \cdot 10^{-4} \text{ mol/cm}^3$$

$$c_R = 9 \cdot 10^{-5} \text{ mol/cm}^3 \qquad /35/$$

$$d = 1 \text{ cm} .$$

which yields

$$\tau_e = 6.62 \cdot 10^{-10} s \; ; \; \tau_d = 7210 \text{ s} . \qquad /35/$$

From the data tabulated by Miller (1966) for the phenomenological coefficients and from the value of M predicted by the Debye-Hückel limit theory (M= -1840 cm^3/mol for $c_0 = 10^{-4}$ mol/cm^3) (Debye and Hückel 1923), we obtain
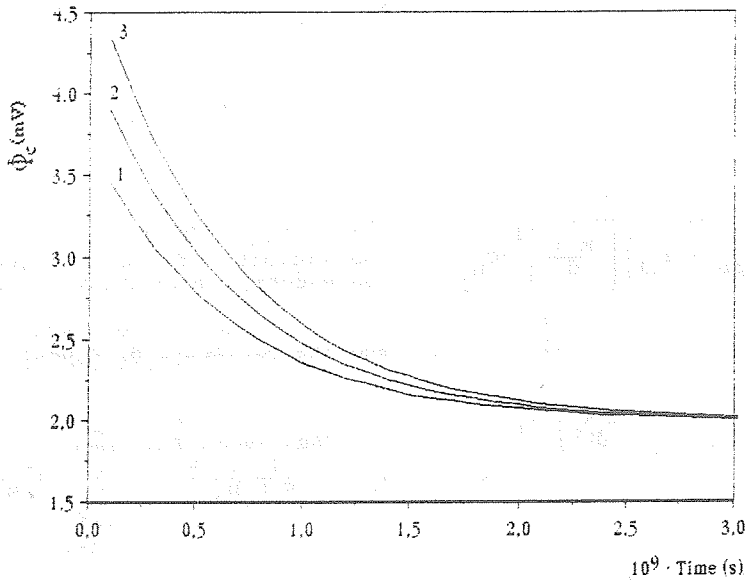

Figure 2

Representation of full cell potential vs. time for the system $LiCl-H_2O$ with $c_L = 1.1 \cdot 10^{-4}$ mol/cm^3 and $c_R = 9 \cdot 10^{-5}$ mol/cm^3 for: 1) $B = 1000$ cm^3/mol; 2) $B = 0$ cm^3/mol and 3) $B = -1000$ cm^3/mol.
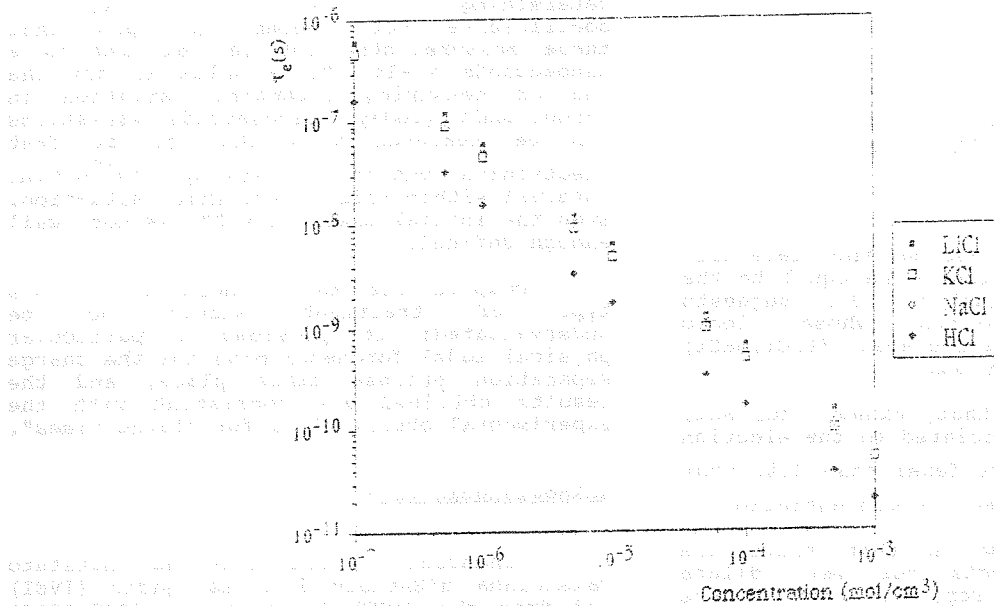
Figure 3

Logarithmic representation of τ_e vs. concentration for four 1:1 binary electrolytes in aqueous solution: LiCl, KCl, NaCl and HCl.
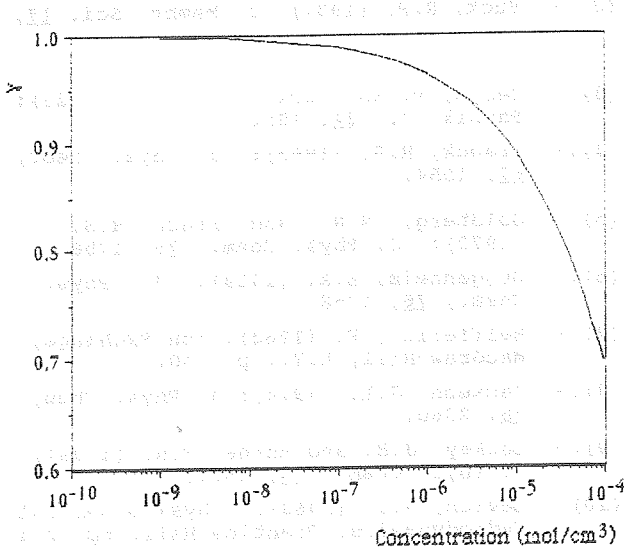

Figure 4

Representation of the mean ionic activity coefficient vs. concentration from Debye-Hückel limit theory for the system LiCl - H_2O.

$$\Phi_c = 6.539 \cdot 10^{-7}(4339 - B) \sum_{\substack{k=1 \\ m=2k-1}}^{\infty} \cdot$$

$$\cdot \frac{(-1)^k}{m} e^{-m^2 t/\tau_d} \left(1 - e^{-t/\tau_e}\right) +$$

$$+ 0.02568(0.1638 - 2 \cdot 10^{-5} B) \quad /36/$$

where B is expressed in cm^3/mol and Φ_c in volts. This series can be easily evaluated for different times with the aid of a computer. Thus, we can obtain the curved of Figure 2, which show that Φ_c has no dependence on B for times greater than $3 \cdot 10^{-9}$ s, approximately.

We can rise the electric relaxation time by considering other electrolytes in other concentration ranges. Looking at the τ_e definition,

$$\tau_e = \frac{\varepsilon\, RT}{F^2(D_1 + D_2)c_0} =$$

$$= 1.86 \cdot 10^{-18}\ \frac{1}{D_1 + D_2}\ \frac{1}{c_0} \qquad /37/$$

where, again, we have assumed the dielectric constant of the solution to be equal to the pure water one. Equation /37/ suggests considering electrolytes whose ionic diffusion coefficients are small (LiCl,NaCl) and very diluted silutions.

Figure 3 shows that, except for HCl, differences in τ_e associated to the election of the electrolyte are fewer than 25%. That is, the important effect is concentration.

The problem now is that there are no "non-ideal" effects for very dilute solutions. (A plane representation of the mean ionic activity coefficient from the Debye-Hückel limit theory shows that only in moderate concentrated solutions remarkable deviations from ideal behaviour can appear (see Figure 4)).

In conclusion, an experimental proof of the present result seems to be quite difficult to achieve. Although a number of thought experiments may be suggested, the problem of determining the moment in which the solution are brought into contact with an accuracy greater than 10^{-9} s seems to be hopeless.

6.- Discussion.-

The linear phenomenological transport equations and Poisson equation have been solved for a free-diffusion liquid junction. The charge separation process has been characterized. Comparison with a previous result obtained by solution of Nerst-Planck/Poisson equations has been made. This previous result has been reinterpretated in terms of the transient of an RC circuit in direct current.

An analysis of the validity of a classical treatment for this process has been made. Though classical analysis is right, the problem considered is not so far from the need of a quantum treatment. That is, in a common sense view, the problem will require a quantum treatment when it concerns to so small distances that specific interactions begins to appear, and the charge separation process involves distances of only 10 Å, approximately.

Equation /34/ and Figure 2 show the theoretical possibility of experimentally determining single-ion activity coefficients, but Figures 3-4 impose that these measurements must be realized in a nanoseconds scale. The problem is not the one of measuring potential variation in nanoseconds (today, picoseconds variations can be measured with the aid of fast electronics),but of determining a 10^{-9}s time interval within this experimenatl situation. Even the initial time, "t = 0", is not well enough defined.

Despite the above shortcoming, this type of treatment should no be undervaluated: it provides a particular physical model for describing how the charge separation process takes place, and the results obtained are consistent with the experimental observations for "large times".

Acknowledgements.-

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