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Bi-ionic potential: Experimental measurements and diffusion coefficients determinations

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ABSTRACT

The bi-ionic potential of charged membranes has been studied theoretically and limiting expression corresponding to not negligible diffusion boundary layer effects has been used. A system formed by two electrolyte aqueous phases bathing an ion-exchange membrane was studied in order to determine the bi-ionic potential, in the case of a ionics cation exchange membrane. The experiments were conducted at different concentration solutions and temperature. To do it a new device was designed and constructed allowing the measuring of potential membrane in the bi-ionic system. The values obtained show a concentration dependence with different maximum values for each temperature. A theoretical model given the bi-ionic potential as a function of diffusion coefficients was used to obtain the values for the K^+ at different temperatures from the corresponding values of Na^+ measured by means a rotating diffusion cell.

Keywords: Ion-exchange membranes; Transport phenomena; Bi-ionic potential

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1. Introduction

The bi-ionic potential, $\Delta\Psi_{BIP,}$ is the potential difference between the aqueous solutions of a bi-ionic system, constituted by an ion-exchange membrane separating two aqueous electrolyte solutions containing, the same co-ion and different counter-ions with respect to the membrane. Fig. 1 outlines the membrane system (membrane+diffusion boundary layers (DBLs)) [1]. The $\Delta\Psi_{BIP}$ is a usual topic in the study of the transport phenomena through charged membranes, not only because the practical importance of the multi-ionic systems in synthetic membranes, but also for its relevance in biological systems. Researches in this field are diverse and include a wide relation of theoretical and experimental studies [2–4].

Most of theoretical treatments presented so far have invoked *at least* one of the following assumptions: (a) Ideal permselectivity of the membrane (i.e., zero co-ion flux) [5]. (b) The effects of the DBLs are negligible [6,7]. (c) The electrical field is constant in the membrane phase (Goldman hypothesis) [8]. (d) The contribution of the Donnan potentials to the bi-ionic potential is negligible [9]. The above assumptions are approximately valid in some practical situations and allow for obtaining very simple limiting expressions for $\Delta\Psi_{BIP}$ without resorting to numerical methods. However, it has been emphasized that the membrane cannot be considered as ideally permselective when the electrolyte concentration of the bathing solutions is of the same order of magnitude as the

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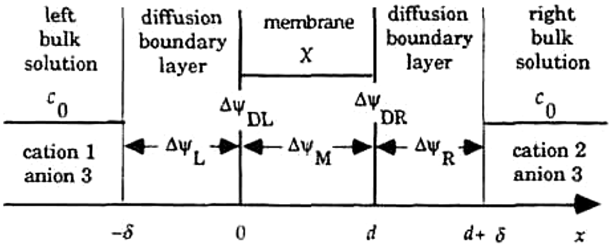

Fig. 1. Schematic view of the membrane system (from [16]).

membrane fixed charge concentration. Also, the DBLs are known to exert a considerable influence on the transport phenomena in multi-ionic systems [10]. It is difficult to eliminate this influence when diluted solutions are employed. Finally, the constancy of the electric field in the membrane phase and that the cancellation of interfacial Donnan potentials appear to be reasonable assumptions when the rate-determining step is the transport through the membrane (i.e. in the case of *membrane control*), but it is not necessarily true when the DBL effects are dominant (*film control*).

In Fig. 1, the ionic transport is considered in the x direction through the membrane that extends from $x = 0$ to d, with two DBLs lying from $x = -\delta$ to 0 and from $x = d$ to $x = d + \delta$.

The paper is aimed to establish the values of the diffusion coefficients of one of the counterions from the corresponding values to another counterion, previously obtained by the employment of a rotating diffusion cell (RDC) [11]. A theoretical model for the bionic potential is developed to do it.

2. Bi-ionic potential theoretical model

Transport is considered in the x direction through the membrane (Fig. 1) in contact with two bulk solution at the same concentration c_0 of different 1:1 binary electrolytes with a common anion. The concentration of charged groups in the membrane is denoted by X and steady-state conditions will be assumed [12,13].

The basic equations describing this problem are the Nernst-Planck equations

$$J_i = -D_i\left(\frac{\mathrm{d}c_i}{\mathrm{d}x}\right) + z_i c_i \frac{\mathrm{d}\Psi}{\mathrm{d}x}, \quad i = 1,2,3\,;\ -\delta < x < 0,\ d < x < d + \delta, \tag{1a}$$

$$J_i = -\bar{D}_i\left(\frac{\mathrm{d}\bar{c}_i}{\mathrm{d}x} + z_i \bar{c}_i \frac{\mathrm{d}\overline{\Psi}}{\mathrm{d}x}\right),\ i = 1,2,3; \quad 0 < x < d, \tag{1b}$$

with subscripts 1 and 2 refer to counterions (cations in our case) and subscript 3 corresponds to the co-ion and where J_i, D_i, c_i and z_i are the flux, diffusion coefficient, and molar concentration and valence of the ith species, respectively. Overbars denote membrane phase. Finally, $\Psi = F\phi/RT$ is the dimensionless electric potential, being ϕ the membrane system potential, F is the Faraday constant, R the gas constant, and T the absolute temperature.

The equation for the (zero) current density

$$J_1 + J_2 - J_3 = 0, \tag{2}$$

and the local electroneutrality assumption

$$c_1(x) + c_2(x) = c_3(x), \qquad -\delta < x < 0, \qquad d < x < d + \delta, \tag{3a}$$

$$\overline{c_1(x)} + \overline{c_2(x)} = \overline{c_3(x)} + X, \qquad 0 < x < d, \tag{3b}$$

Eqs. (1)–(3) must be solved with the boundary conditions

$$c_1(-\delta) = c_2(d + \delta) = c, \tag{4a}$$

$$c_2(-\delta) = c_1(d + \delta) = 0. \tag{4b}$$

Also, according to the well-known Donnan equilibrium [14,15], both the ionic concentration and the membrane system potential are assumed to be discontinuous at the membrane/DBL interfaces.

The use of Eqs. (3) leads to a simple analytical solution giving in the membrane phase,

$$\frac{J_1}{\overline{D_1}} + \frac{J_2}{\overline{D_2}} + \frac{J_3}{\overline{D_3}} = -2\frac{\mathrm{d}\bar{c}_3}{\mathrm{d}x} - X\frac{\mathrm{d}\overline{\Psi}}{\mathrm{d}x}, \quad \text{(membrane)} \tag{5}$$

which can be integrated to give

$$2\left[\overline{c_3(d)} - \overline{c_3(0)}\right] + X\delta\psi_{\text{diff}} + (\bar{j}_1 + \bar{j}_2 + \bar{j}_3)d = 0 \tag{6}$$

where $\bar{j}_i \equiv J_i/\overline{D_i}$ and $\Delta\Psi_{\text{diff}} \equiv \overline{\Psi(d)} - \overline{\Psi(0)}$ is the diffusion potential drop in the membrane phase. In the DBLs, the sum of the Nernst-Planck equations shows that the co-ion concentration gradient is constant (take $X = 0$ in Eq. (5) and consider magnitudes referred to the DBLs), and hence

$$c_3(0) = c_0 - \frac{j_1 + j_2 + j_3}{2}\delta, \tag{7a}$$

$$c_3(d) = c_0 + \frac{j_1 + j_2 + j_3}{2}\delta, \tag{7b}$$

where $j_i \equiv J_i/D_i$.

The diffusion potential drop in the membrane is easily calculated by adding $(1-\overline{\Gamma})/2$ times Eq. (5) to Eq. (1b) for $i = 3$, with the result [16]

$$\Delta\Psi_{\mathrm{diff}} = \overline{\Gamma} \ln \frac{\overline{c_3(d)} + X(1-\overline{\Gamma})/2}{\overline{c_3(0)} + X(1-\overline{\Gamma})/2}. \tag{8}$$

The corresponding equations for the DBLs are

$$\Delta\Psi_{\mathrm{L}} = \Psi(0) - \Psi(-\delta) = \Gamma \ln \frac{c_3(0)}{c} \tag{9}$$

and

$$\Delta\Psi_{\mathrm{R}} = \Psi(d+\delta) - \Psi(d) = \Gamma \ln \frac{c}{c_3(d)}, \tag{10}$$

where

$$\Gamma \equiv \frac{j_1 + j_2 - j_3}{j_1 + j_2 + j_3} \tag{11a}$$

and

$$\bar{\Gamma} \equiv \frac{\bar{j}_1 + \bar{j}_2 - \bar{j}_3}{\bar{j}_1 + \bar{j}_2 + \bar{j}_3}. \tag{11b}$$

The bionic potential is now calculated as the sum of the different potential drops through the system [17,18]

$$\Delta\Psi_{\mathrm{BIP}} = \Delta\Psi_{\mathrm{L}} + \Delta\Psi_{\mathrm{DL}} + \Delta\Psi_{\mathrm{diff}} + \Delta\Psi_{\mathrm{DR}} + \Delta\Psi_{\mathrm{R}} \tag{12}$$

All these potential drops are schematically represented in Fig. 1.

When very low electrolyte concentration (c_0) vs. electric charge concentration in the membrane (X) can be assumed the concentration of co-ions in the membrane phase is very small, and thus the potential drop in this phase must be negligible, for any potential drop would lead to an important electric current due to the high concentration of counterions. At both sides of the membrane, the co-ion concentrations can be approximated as $\bar{c}_3 \approx c_3(0)^2/X$ and $\bar{c}_3 \approx c_3(d)^2/X$, so that the sum of the Donnan potentials is

$$\Delta\Psi_{\mathrm{DL}} + \Delta\Psi_{\mathrm{DR}} = \ln \frac{\overline{c_3(0)}c_3(d)}{c_3(0)\overline{c_3(d)}} \approx \ln \frac{c_3(0)}{c_3(d)} \tag{13}$$

while the sum of the potential drops in the DBLs is given by Eqs. (9) and (10) as

$$\Delta\Psi_{\mathrm{L}} + \Delta\Psi_{\mathrm{R}} = \Gamma \ln \frac{c_3(0)}{c_3(d)}, \tag{14}$$

and therefore, the bi-ionic potential can be readily obtained as

$$\Delta\Psi_{\mathrm{BIP}} \approx \Delta\Psi_{\mathrm{L}} + \Delta\Psi_{\mathrm{DL}} + \Delta\Psi_{\mathrm{DR}} + \Delta\Psi_{\mathrm{R}} = (1+\Gamma) \ln \frac{c_3(0)}{c_3(d)}, \tag{15}$$

If the membrane permeability to co-ions is very small, the co-ion flux results to be negligible when compared to the counterions fluxes, i.e. $|J_3| << |J_1| \approx |J_2|$ and so that $\Gamma \approx 1$ (see Eq. (11a)), it follows that

$$\Delta\Psi_{\mathrm{L}} + \Delta\Psi_{\mathrm{R}} = \ln \frac{c_3(0)}{c_3(d)}, \tag{16}$$

which amounts to assume that co-ions are in equilibrium in the DBLs. However, the co-ions cannot be considered to be in equilibrium in the membrane phase because the co-ion flux and the co-ion concentration are very small there, and then the three terms in Eq. (1b) for $i = 3$ are of the same order of magnitude.

To obtain the value of $\Delta\Psi_{\mathrm{BIP}}$, the counterions must be considered. The sum of Eqs. (1) for $i = 1$ and $i = 2$ gives

$$\frac{\mathrm{d}u}{\mathrm{d}x} + u\frac{\mathrm{d}\Psi}{\mathrm{d}x} = -J_3 \approx 0 \tag{17a}$$

and

$$\frac{\mathrm{d}\overline{u}}{\mathrm{d}x} + \overline{u}\frac{\mathrm{d}\overline{\Psi}}{\mathrm{d}x} = -J_3 \approx 0, \tag{17b}$$

where $u \equiv D_1c_1 + D_2c_2$ and $\overline{u} \equiv \overline{D_1c_1} + \overline{D_2c_2}$. Since we have shown above that there can be no potential drop in the membrane, Eq. (17b) implies that the counterion concentration gradients in the membrane are also negligible, and therefore

$$\overline{c_i(0)} \approx \overline{c_i(d)}, \quad i = 1, 2. \tag{18}$$

Thus, the sum of the two Donnan potentials is

$$\Delta\Psi_{\mathrm{DL}} + \Delta\Psi_{\mathrm{DR}} = \ln \frac{c_1(0)\overline{c_1(d)}}{c_1(d)\overline{c_1(0)}} \approx \ln \frac{c_1(0)}{c_1(d)} \approx \ln \frac{c_2(0)}{c_2(d)} \tag{19a}$$

having made use of Eq. (18). Also, the sum of the potential drops in DBLs can be obtained, by using Eqs. (17), as

$$\Delta\Psi_{\mathrm{L}} + \Delta\Psi_{\mathrm{R}} \approx \ln \frac{D_1u(d)}{D_2u(0)}. \tag{19b}$$

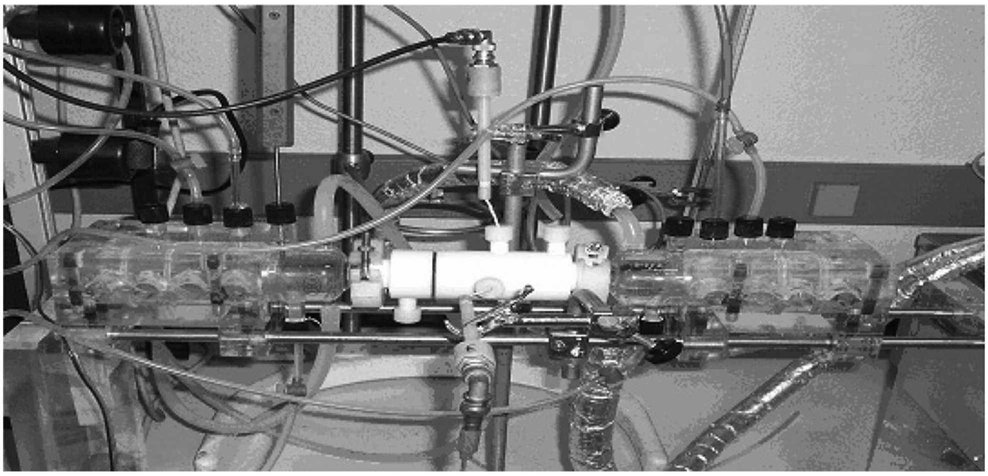

Fig. 2. Electrochemical measuring cell view. In white the membrane holder: part left is screwed in part right fixing the membrane between two measuring ion selective electrodes (ISEs). The glass chambers at both sides of holder are jacketed and contain the external electrolyte solutions in contact with the membrane.

Finally, the bionic potential is given by

$$\Delta\Psi_{\mathrm{BIP}} \approx \Delta\Psi_{\mathrm{L}} + \Delta\Psi_{\mathrm{DL}} + \Delta\Psi_{\mathrm{DR}} + \Delta\Psi_{\mathrm{R}} = \ln\frac{D_1}{D_2} \qquad (20)$$

3. Experimental setup

Our measuring bi-ionic potential device is shown in Fig. 2: two glass chambers containing the aqueous solutions are connected to the membrane holder (white). The complete experimental setup is outlined in Fig. 3. The membrane is bathed by two bulk solutions with the same concentration of different 1:1 binary electrolytes with a common anion and where steady-state conditions are assumed [19]. The experiments were accomplished with NaCl and KCl solutions and therefore the co-ion is Cl^-. The solutions were prepared from bi-distilled, de-gassed and de-ionized water treated by reverse osmosis in a Milli-Q Plus (resistivity of 18.2 MΩ). One cationic

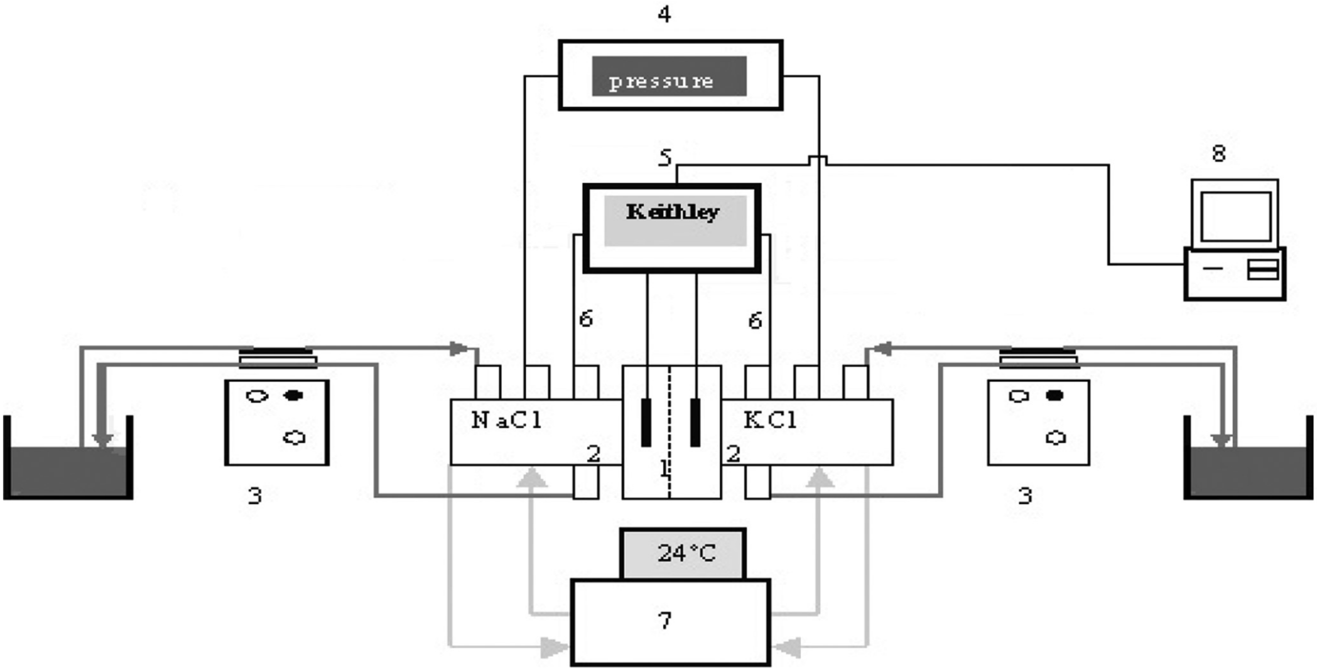

Fig. 3. Experimental setup: 1. Membrane holder and ISEs. 2. External solutions chambers. 3. Peristaltic pumps. 4. Differential manometer. 5. Multimeter. 6. Temperature probes. 7. Thermostatic bath. 8. PC.

ion-exchange membrane *Ionics* (CR61AZL, with a porosity of 0.0035 pores/mm^2 and an exchange capacity of 2.10 mequiv/g) has been used. This membrane is a cross-linked sulfonated copolymer of vinyl compounds cast in homogeneous films on synthetic reinforced fabrics. According to the data provided by manufacturer, this membrane has 1.6×10^{-3} mol/cm^3 sulfonated groups and it is mainly hydrophilic. In this way, the values corresponding to X is very greater than the values corresponding to c_0, ranging between 10^{-6} and 10^{-5} mol/cm^3 in our experiments. The solutions were employed at the same temperature, to avoid thermal gradients and placed at both sides of the membrane in two jacketed glass containers, whose temperature was controlled (± 0.1°C) with the help of a thermostatic bath, whose liquid was continuously flowing through the jackets. Temperature was measured by J thermocouples.

3.1. Electrochemical measuring cell

This cell is subdivided in three compartments (Fig. 2): the membrane holder containing the membrane and two reference electrodes and two thermal probes, and at both ends of the membrane holder are joined two jacketed glass chambers for the external electrolyte solutions. Toroid gaskets are inserted between each compartment to ensure the cell tightness.

The membrane cell is constituted by two Teflon block A and B having 13.5 cm total length and bored in its horizontal central axis with a cylinder vein of 2.5 cm in diameter. The membrane is placed inside A and adjusted by a set of O-rings while the part B is screwed in A, fixing the membrane which remains between two inlets housing the measuring electrodes at both side of the membrane. Stirring and maintaining concentration solutions near the membrane surfaces was achieved by constantly flowing electrolyte through solutions chambers.

The glass containers of the aqueous phases (2 in Fig. 3) with volume of 41 cm^3 approximately were provided with Perspex jackets, in order to control the temperature in the solutions. They are provided with pipes to fill and empty besides inlets for pressure and temperature sensors, so as for the inflow–outflow of the solutions. An other circuit was used for the recirculation of thermostatic liquid through the jackets. The capacity of these jackets was greater than those of the chambers, to ensure a more effective thermal control.

To guarantee the homogeneity of the solutions at both sides of the membrane, a recirculation system was designed such as illustrated in Fig. 3. Each compartment was connected through the appropriate inlet to a 2 l reservoir via a peristaltic pump Gilson Miniplus-2. The components were connected by means of 5 mm internal diameter thick-walled PVC tubing. Both circuits were closed from the atmosphere, and the circulating rate was up to 1 l/h, with a velocity of 1.4 cm/s, giving a laminar flow in the circuits.

Once the chambers filled with the corresponding solutions, the circulation circuits were started. The aqueous solutions were extracted from their reservoirs by pumps, introduced in the corresponding containers and flowing through bottom outlet of these chambers towards the reservoirs.

3.2. Differential manometer

The pressure different between the solutions chambers was maintained at zero value and measured by a manometer Digitron P600 (4 in Fig. 3). The peristaltic pumps give small amplitude pressure pulses with oscillatory response around zero value, negligible in practice. This manometer has a full scale of 1,000 mBar with a resolution of 0.1 mBar and was connected to the chambers by means of tubes 3 mm internal diameter and 35 cm length. The digital output of the manometer was connected to a data acquisition and control system.

3.3. Bi-ionic potential device

The resulting electrical potential difference through the membrane system was measured by two silver/silver chloride electrodes [20]. Potential difference between these sensors was measured by means of a multimeter *Keithley* 2700 through a multiplexed input and whose output *RS232* was connected to a computer for storage and treatment of results. This device is a hybrid system combining a digital multimeter (current, voltage, temperature, etc.) with some of the functions of a data acquisition systems. A suitable software allows the management of all the data obtained by a PC.

3.4. Bi-ionic potential results

In all our experiments, aqueous solutions of NaCl and KCl at the same concentration and temperature were used on each side of the membrane. In this way it is possible to study the behavior of the bi-ionic potential with respect to the temperature, and so we have considered a temperature range from 20 to 50°C with intervals of 10°C, at every concentration value.

On the other hand, the solutions were prepared at the following concentrations: 0.001, 0.0025, 0.0050, 0.0075, 0.010 M. For every one of these temperatures, measurements of bi-ionic potential were accomplished, at each one of the considered concentrations. Thus, it is possible to study the behavior of the potential with respect to concentration.

Table 1
Bi-ionic potential for the system NaCl(ac) | *Ionics* membrane | KCl (ac) at different temperatures and concentrations

	Temperature (°C) (±0,1)			
Concentration (M) (±0.0001)	20.0 Bi-ionic Potential ($\times10^{-2}$ V) (±0.01)	30.0 Bi-ionic Potential ($\times10^{-2}$ V) (±0.01)	40.0 Bi-ionic Potential ($\times10^{-2}$ V) (±0.01)	50.0 Bi-ionic Potential ($\times10^{-2}$ V) (±0.01)
0.0010	5.60	5.79	5.62	5.28
0.0025	7.60	7.56	7.38	7.11
0.0050	7.06	8.07	10.38	12.11
0.0075	6.81	5.86	6.69	9.05
0.0100	4.74	4.70	4.70	4.70

Experiments were in steady state, what required ten minutes delay in starting measurements in all cases, to ensure this situation. The time interval for measuring potential was fixed in 5 s, what was programmed by the multimeter. Finally, the results were obtained from the measurements, as an average value calculated by mean of a PC program.

Table 1 illustrates the potential bi-ionic values obtained for the different temperature at every concentration, when solutions of NaCl and KCl are placed at both sides of the *Ionics* membrane. Fig. 4 shows these values. We can see the potential has a very variable behaviour depending on the concentration of the solutions, reaching a maximum value, depending on temperature. In all cases, maximum values are found in the same zone of concentration, around 0.005 M, although values found for 50°C which is greater than those values corresponding to the other temperatures.

The study of the potential bi-ionic values with respect to temperature shows no significant changes, excepting in the case of 0.005 and 0.075 M for which the potential increase lightly with temperature. Fig. 5 shows this behaviour.

3.5. Diffusion coefficients determination

The object is the determination of the diffusion coefficients of the K^+ from the corresponding values of the Na^+ and the bionic potential measurements. The Na^+ coefficient were obtained by employment of a RDC (Fig. 6). The study was accomplished for the system HCl (ac)/*Ionics* CR61AZL membrane/NaCl (ac). The membrane separating feed and receiving aqueous solutions was mounted on the bottom of a hollow rotating cylinder containing HCl aqueous solution. This cylinder can turn at different constant rotating

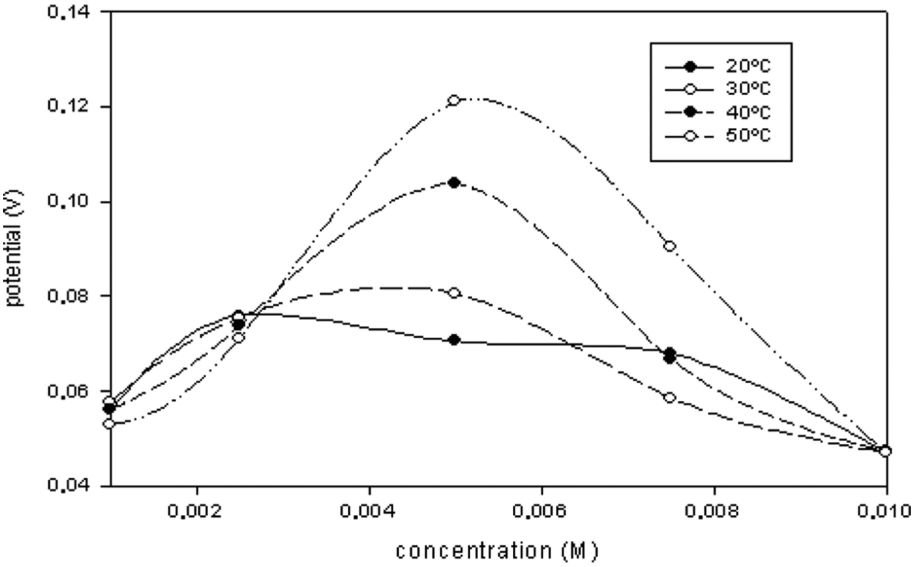

Fig. 4. Bi-ionic potential vs. concentration for the system NaCl(ac) | *Ionics* membrane | KCl (ac) in the temperature range (20–50)°C.

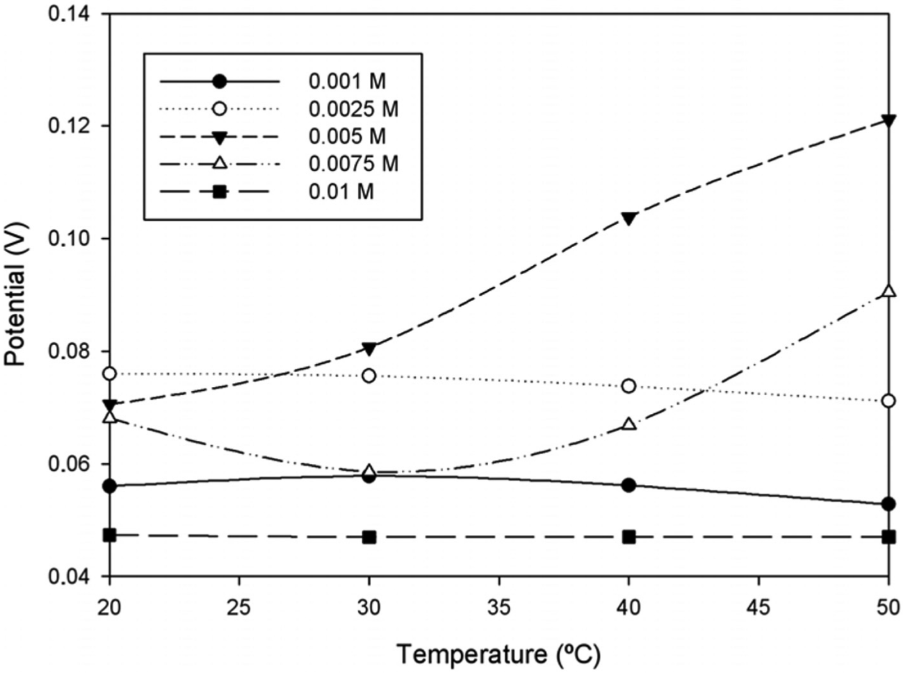

Fig. 5. Bi-ionic potential vs. temperature for the system NaCl(ac) | *Ionics* membrane | KCl(ac), at different concentrations over the range 1×10^{-3}–1×10^{-2} M.

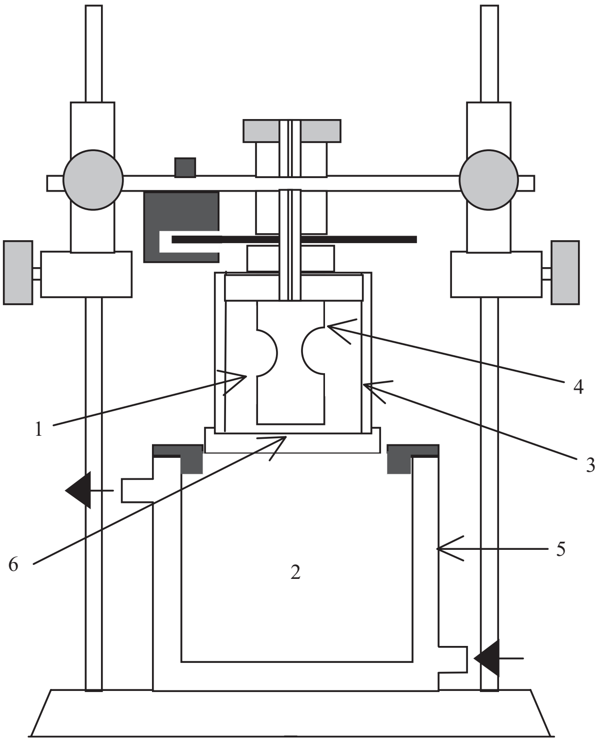

Fig. 6. RDC device: 1. Inner compartment. 2. Outer jacketed compartment. 3. Rotating cylinder. 4. Stationary cylinder. 5. Stationary temperature compartment. 6. Membrane.

frequency over the range 2.5 to 12.5 Hz and was partially submerged in the other aqueous solution contained in a fixed and jacketed vessel. The transport was studied over to range of temperatures between 20 and 50°C.

Table 2 shows the values obtained for the Na^+ diffusion coefficient in an aqueous solution at 0.005 M with a RDC (rotating frequency: 2.5 Hz). The measurement of the bi-ionic potential accomplished in our device together with the equation (20), with 1 as K^+ and 2 as Na^+, allows us the determination of the other counterion diffusion coefficient (K^+ in our case). The results are also illustrated in Table 2. This method can be used at other different concentrations and temperatures to give the corresponding coefficients. These values are

Table 2
Diffusion coefficients of K^+ in KCl aqueous solutions at 5×10^{-3}M from bi-ionic potential measurements at different temperatures, from the corresponding values of Na^+ obtained by RDC method

θ (°C) ($\pm$ 0.1)	D_{Na^+} ($\times10^{-5}$ cm^2/s)	D_{K^+} ($\times10^{-5}$ cm^2/s)
20	1.4 $\pm$ 0.2	1.5 $\pm$ 0.1
30	1.6 $\pm$ 0.1	1.7 $\pm$ 0.1
40	1.9 $\pm$ 0.2	2.1 $\pm$ 0.1
50	2.2 $\pm$ 0.2	2.5 $\pm$ 0.1

of the same order that quoted in the literature for aqueous solutions at infinite dilution [21] and these obtained by Donnan Dialysis Study [22,23].

4. Conclusions

In this paper we have reported about an experimental setup designed to measure the bi-ionic potential established through the membrane system, when two aqueous electrolytic solutions with a common co-ion are placed at both sides of the membrane. In our case solutions of NaCl and KCl were used. The bi-ionic potential of charged membrane has been studied theoretically. An analytical solution to the Nernst-Planck equations describing the multiionic transport through the charged membrane and the DBLs has been obtained. One limiting expression, corresponding to low bathing solution concentration has been used.

The experimental study of the bi-ionic system with the temperature changes (range: 20–50°C) and concentration (range: 0.001–0.075 M) was carried out. In all studied cases, the potential had a variable behaviour with the concentration imposed, despite the fact that qualitative behaviour is similar in all the cases studied. Maximum values depending on concentration were registered followed for a quasi-steady response. On the other hand, it has been established a simple method for obtaining cationic coefficients of diffusion at different temperatures from the bi-ionic potential measurements using results obtained by a RDC for a pattern cation.

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