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Transport of non-associated electrolytes in acrylamide hydrogels

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Diffusion of non-associated electrolytes (LiCl and KCl) in different hydrogels has been studied to identify the mechanism of electrolyte interaction with the structure of hydrogels and its dependence on electrolyte concentration and thermodynamic features of the electrolyte. Hydrogel membranes have been prepared from acrylamide (AAm) using N,N'-methylene-bis-acrylamide (MBAAm) as the cross-linker. Properties of membranes have been altered varying the content of cross-linker. Integral diffusion coefficients of potassium chloride and lithium chloride in the hydrogel membranes have been compared with mutual diffusion coefficients of those electrolytes in aqueous solutions. The study of electrolyte diffusion was supported by data on water solubility in hydrogels (degree of swelling, and sorption and desorption isotherms) showing dependence of electrolyte diffusion coefficient on water content inside polymer matrix. Thermodynamic study showed irreversible character of the sorption of solutes, probably due to acidic hydrolysis of amide groups of gels. The main features, which characterise properties of aqueous solution of strong electrolytes, remain in polymer matrix thus defining diffusion coefficients and other parameters representative of electrolyte transport in polyacrylamide hydrogels.

1. INTRODUCTION

The study of hydrogels receives considerable attention due to a number of applications as drug release [1], soft contact lenses [2], agriculture [3], filters for water purification [4], separation materials for chromatography and electrophoresis [5], showing the technological and fundamental interest in polymer gels. The transport of electrolytes in polymeric materials [6-8] have been studied to develop the knowledge of the transport mechanism of such specific solutes, as well as to study the properties of the polymers, as for example their degradation and stabilisation, when submitted to electrolytic media. Moreover, the mechanism of electrolyte transport, which may involve a variety of interactions between the system constituents, must be taken into account for proper designing novel polymeric systems. The hydrogels represent those polymers where the interaction of solute molecules with the molecular structure of the gel [9] is very important.

There are a number of models describing how diffusion coefficients (either Fickian or thermodynamic) of solutes in hydrogels vary with water concentration, polymer volume fraction, etc. An overview of these models and experimental data was recently made by Amsden [10]. It has proven that the development of any specific hydrogel subject to application in electrolyte-containing media requires clear understanding of the mechanism of electrolyte diffusion in polymer and adequate modelisation of the diffusion process. For example, a number of models were derived from the study of organic solutes [11,12]. It is not clear whether these models are applicable to the diffusion of strong electrolytes. Once adequate model is selected or developed we need a set of measurable parameters to validate such a model on a quantitative basis.

The lithium and potassium chlorides show different hydration features on the water structure [13]. Therefore the interactions water-ion, water-water and ion-ion (usually related to the interionic distance) are very important to describe the transport phenomena of such electrolytes in aqueous solutions [14, 15]. The aim of this work is to (i) characterise transport of the above electrolytes in hydrogels comparing sorption, diffusion and permeability data, (ii) to evaluate how water-ion, water-water and ion-ion interactions affect the features of the diffusing media, as well as to study the effect of the cross-linking on the interactions balance.

A quantitative explanation for the experimental data is attempted taking into account the free volume theory [16,17] as well as the specific features to the electrolyte solutions.

2. EXPERIMENTAL

2.1. Solutions and membranes
The following chemicals were used: acrylamide (Riedel-de Häen), N,N'-methylene-bis-acrylamide (Merck), sodium persulphate (Fluka AG), and lithium and potassium chloride (Riedel-de Häen). All chemicals were of *pro-analysis* quality and were used without further purification. The electrolyte solutions were prepared after drying the electrolytes until constant weight at 110 °C (KCl) and 180 °C (LiCl) [18].

Pre-gel homogeneous solutions of acrylamide (AAm) 2.5 M with 1 % and 5 % (mol/mol) of N,N'-methylene-bis-acrylamide (MBAAm), and 1 % (w/v) of initiator, $Na_2S_2O_8$, were prepared. Membranes were produced dropping the pre-gel solution inside two glass sheets separated by plastic rubber gasket. Spring clips were used to hold the glass sheets together. After this procedure, the mould was placed in the oven at 50 °C for 2 hours. The hydrogel membrane was then removed from the mould, placed between two plastic sheets, and stored inside an exsiccator at about 100 % humidity in order to maintain its water content. The polymerisation occurs *via* free-radical co-polymerisation of the AAm and MBAAm [19].

2.2. Equilibrium studies
Different samples of the same membranes were cut, weighed and immersed in water at 25 °C until equilibrium was reached (14 days). When the hydrogel samples reach the equilibrium in water, they were transferred from water to each of the salt solutions, from 0.1 M to 1.0 M, with a volume of 200 mL, and left to reach equilibrium (14 days). After this time the membranes were removed, weighed and each one was transferred to a 100 mL of water volumetric flask, to calculate the concentration of the electrolyte that may dessorve the hydrogel matrix, C_{SS}. The approach to equilibrium was controlled gravimetically (Sartorius analytical balance, with a resolution of 0.1 mg) and when necessary the volume of the swollen membrane, V, was measured. Each experiment was repeated at least 3 times.

The swelling degree of the gel, Q, in salt (water and aqueous salt) solutions is calculated from:

$$Q = \text{mass of swollen gel} / \text{mass of xerogel} \tag{1}$$

The concentration of water in the gel, C_W, is computed through:

$$C_W = n_W / V \tag{2}$$

where n_W is the amount of substance of water inside hydrogel and V is the volume of the membrane in dm^3.

The concentration of the electrolyte sorbed by the membrane (C_S as in eq. 3) was obtained by measuring the concentration of salt in aqueous solution of a volume V' prior (c_0) and after (c_∞) the swelling experiments, using a conductivity instrument (YSI 3200).

$$C_S = (c_\infty - c_0) \, V' / V \tag{3}$$

Measuring the amount of electrolyte n_D that leaches the membranes, and comparing it with the amount of salt entering the matrix (n_S), we may compute the concentration of the desorbed salt

$$C_{SS} = (n_S - n_D) / V \tag{4}$$

The average values of C_{SS} and C_S were obtained by three independent measurements.

2.3. Diffusion in aqueous solutions

The mutual diffusion coefficients of the non-associated electrolytes in aqueous solutions were obtained using an open-ended conductimetric capillary cell. Because this technique is described well enough in the literature [20] only a synopsis is given here. The equipment basically consists of two capillaries, each closed at one end by a platinum electrode and positioned one above the other with the open ends separated by a distance of about 10 mm, and a third platinum electrode positioned in the middle. The upper and lower capillaries, originally filled with electrolyte solution of concentration 0.75 c_b and 1.25 c_b, respectively, are surrounded by electrolyte solution of concentration c_b. The mutual differential diffusion coefficient, D_0, is obtained by measuring the electrical resistance of the solution inside the top and bottom capillaries as a function of time [20]. The open-ended capillary cell can be used coupled with two different apparatus: manual and automatic [21]. We present here results of differential diffusion coefficients of LiCl and KCl from 0.1 to 1 M, obtained using the manual system of the technique. The measurement of diffusion coefficients of the electrolytes in free diffusion was performed using a cell designed differently from the original [22], eventually to allow measurements of thermodynamic diffusion coefficients of electrolytes in polymeric membranes. The modifications carried out on the manual system of the cell [21] allow studying the diffusion of electrolyte aqueous solutions in a large concentration range (0.1 – 2.0 M). Although the improvements seems to produce a slight decrease in the precision of the D_0 [23-26] (see Table 2 in the Results and Discussion section), probably caused by the increase in electrical noise which causes a loss of sensitivity in the oscilloscope image, the D_0 values

show a good agreement with those obtained using other reliable techniques [27, 28], and the imprecision on the average mutual diffusion coefficients is still generally lower than 1 %.

2.4. Permeability studies

Permeability of electrolytes in polyacrylamide gels was measured using earlier reported cell [8] (Figure 1) consisting of two compartments filled with electrolyte solution (CA) and water (CB), respectively. The hydrogel membrane (M), previously swollen in water up to equilibrium, was placed between the two cells. Silicone was used for sealing the membrane to ensure hermetic interfaces. Both compartments were stirred with helicoidal stirrer (A) at 220 rpm.
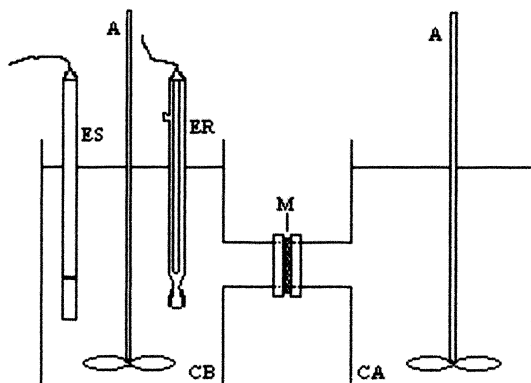

Fig. 1. Schematic representation of permeability cell. M=hydrogel membrane. of thickness l is held between two compartments CA and CB; CA=compartment filled with the electrolyte solution; CB=compartment filled with water; A=stirrer; ES=chloride ion selective electrode; ER=reference electrode.

The electrolyte permeation through membrane was monitorised using a selective chloride electrode (ES) coupled to a pH Meter Methrom 645, with a 0.1 mV resolution. The electrode was calibrated with standard sodium chloride solutions before each experiment. The data were recorded after reaching the steady state. The concentration in the compartment CB (c_{CB}) did not exceed 10^{-3} M, approximately 2-3 orders of magnitude lower than the initial electrolyte concentration in the compartment CA (c_{CA}). At that range ($c_{CB} < 10^{-3}$ M), the selective electrode shows a very high sensitivity, producing an error smaller than 0.4 % on the electrode potential measurement (taking into account the resolution of the apparatus). At the same time the selective electrode gives us a direct measurement of the permeation of chloride ions and, due to the electroneutrality principle, of the electrolyte as well. The cell was thermostated at 25 °C and experiments were performed using electrolyte concentrations in the range of 0.1 - 1 M.

Assuming a Fickian diffusion and the initial and boundary conditions

$$C(0,t) = C_{CA} = Kc_{CA}; \quad C(l,t) = 0, \quad C(x,0) = 0 \tag{5}$$

where C_{CA} is the initial concentration of the electrolyte in the membrane and K is partition coefficient. The effective permeability coefficient, P, was calculated from the following equation

$$P = J \, l \, / \, c_{CA} \tag{6}$$

where l is the thickness of the hydrogel membrane, measured after each experiment, J is the steady-state flux and c_{CA} is the initial concentration of the electrolyte solution (assumed constant during an experiment). The J can be calculated from the trend line slope k

$$J = k \, V_{CB} \, / \, A \tag{7}$$

where V_{CB} (= 180 mL) is the volume of solution inside cell CB and A = 1.5394 cm^2.

The mean values of P were calculated from a set of experiments (at least 3). The standard deviation of the average values is in all the cases ≤ 10 %. This error is acceptable once different error sources may arise during an experiment as, for example, the heterogeneity of the hydrogels [19]. The sealing of the membrane to the cell as well as the permeation area is another important factor: a decrease of 5 % in the permeation area can result in an increase of permeability coefficient of 10 %.

To prevent contribution of a convection flux to the mass transfer, the stirring rate of the solutions was tested. In a control experiment, designed to estimate the possible contribution, there was no stirring in cell CA (electrolyte cell) and very slow stirring in CB (water cell). Comparing the results with those obtained in "normal" conditions, the average velocity of the particle [29] was estimated to be approximately 8 x 10^{-8} m s^{-1}. Once it is not possible to increase the stirring velocity we shall have to take into account the possible formation of the Nernst layer, and its consequences on the permeability coefficients. The Nernst layer thickness, l_N, was estimated, considering a set of experiments of the system KCl (0.3 M)/gel II, according to

$$c_{CA} \, / \, J = (1 \, / \, P) + (l_N \, / \, D_0) \tag{8}$$

where D_0 is the diffusion coefficient of the electrolyte in aqueous solution. The permeability coefficient, calculated using eq. (8), is similar (within the experimental error) to that obtained equation (6). Therefore, in our case the Nernst layer can be neglected as providing no effect on the calculation of the permeability coefficient in the membrane.

3. RESULTS AND DISCUSSION

3.1. Equilibrium studies

Table 1 presents the experimental values of different parameters, which may characterise the effect of cross-linking on the properties of gel when it is in equilibrium with water. The swelling degree, Q, decreases with an increase in cross-linking, as a consequence of a more rigid structure (gel II) followed by a difficult access of the water to the polar groups of the polymeric chain. This does not agree with the variation of the polymer density, ρ. If we compare water concentration in initial materials (after synthesis: C_W') and in swollen hydrogels (C_W), and volume ratio (β) of hydrogels at these reference stages, we may conclude that only the PAAm-gel, cross-linked at 1 % (gel I), actually swells when exposed to water,

whereas that cross-linked at 5 % does not.

Table 1
Parameters characterising equilibrium water content in polyacrylamide with different percentage of cross-linker: 1 % (gel I) and 5 % (gel II) at 25 $^{\circ}$C

Gel	$Q \pm s$/ (w/w)	$\rho \pm s$ / (g cm^{-3})	$C_W' \pm s$ / M	$C_W \pm s$/ M	$\beta \pm s$
I	11.6 ± 0.21	0.36 ± 0.03	48 ± 1	44 ± 1	1.9 ± 0.1
II	5.76 ± 0.01	0.24 ± 0.01	47 ± 1	30 ± 1	1.00 ± 0.02

Q=degree of swelling of the gels, ρ=polymer density (calculated assuming that the density of water in the hydrogel is equal to 1 g cm^{-3}); C_W'=water concentration in gel after synthesis; C_W=water concentration in gel at equilibrium; β=volume ratio between swollen and initial hydrogels; s=standard deviation of three independent measurements.

The measurement of swelling degree of both gels at equilibrium with concentrated aqueous solutions of KCl and LiCl (Figures 2 and 3) shows an osmotic effect produced by these electrolytes. Swelling degree (Q) increases with the electrolyte concentration, more significant in gel I. These Q variations are in good agreement with experimental results obtained in similar experiments on study of polyacrylamide gels in NaCl solutions [30]. Saito showed that it happens at electrolyte concentrations where ion-solvent and ion-polymer interactions cannot be neglected [31]. Such behaviour is also observed in ampholytic gels where the salt presence tends to screen the attractions between the gel ionic groups and consequently a chain expansion occurs [32, 33].
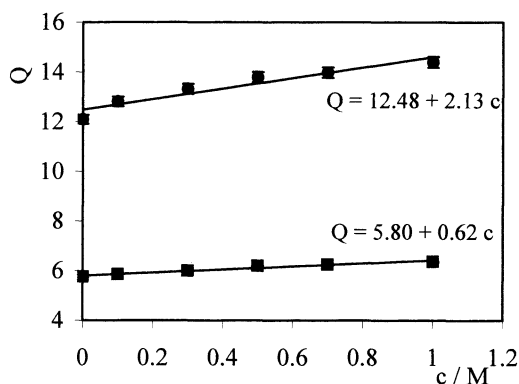

Fig. 2. Degree of swelling (Q) of polyacrylamides with 1 % of MBAAm (●) and with 5 % of MBAAm (■) with in aqueous KCl solutions at 25 $^{\circ}$C.
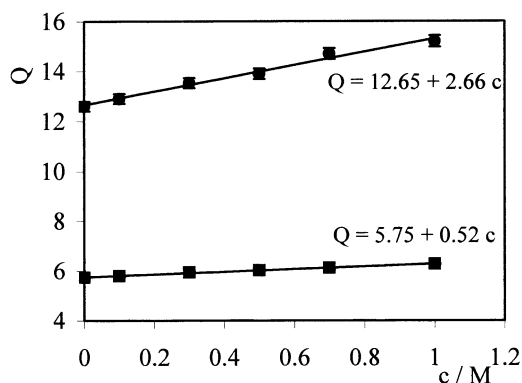
Fig 3. Degree of swelling (Q) of polyacrylamides with 1 % of MBAAm (●) and with 5 % of MBAAm (■) with in aqueous LiCl solutions at 25 °C.

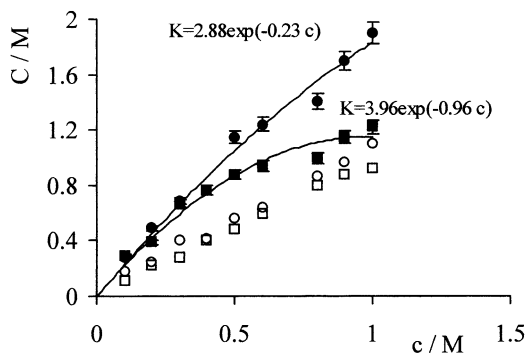Figures 4 and 5 show the isotherms of the KCl and LiCl, respectively, in both hydrogels.

Fig. 4. KCl sorption (black points) and desorption (white points) isotherms in polyacrylamides with 1 % of MBAAm (●, ○) and with 5 % of MBAAm (■, □), at 25 °C.

The sorption of LiCl is similar in both gels. This can be justified by the highly stabilised ion-water and ion-ion (ion-pair formation) interactions that characterise the Li^+ aqueous solutions. This is a consequence of the high charge density of the lithium ion as well as of the positive hydration [13]. The opposite effect produced by potassium ions on the water structure is characterised by a water-breaker structure. It may justify the dependence of electrolyte partition coefficient (K) on the electrolyte concentration. In more hydrophilic gel KCl sorption isotherms show an essential K dependence on the electrolyte concentration c, probably due to the balance between the ion-pair formation at higher KCl concentrations [34], and the water-breaker structure features of the potassium ions lower concentrations. The latter feature results in water-water interaction predominance in comparison ion-water interactions. That balance is enhanced (higher K dependence on the KCl concentration) by the decrease of water

concentration in the gel II. These sorption processes may be accompanied by the occurrence of ion-polymer interactions, which can justify the high K values as well as the irreversible sorption of all systems.
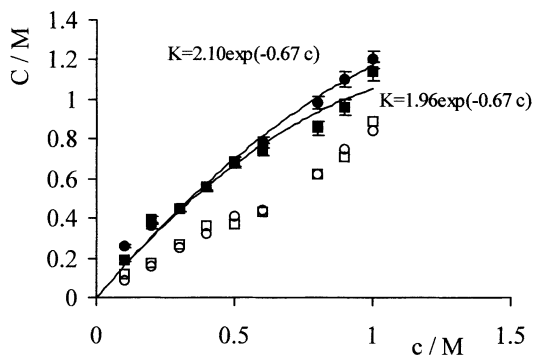

Fig. 5. LiCl sorption (black points) and desorption (white points) isotherms in polyacrylamides with 1 % of MBAAm ($\bullet$, $\circ$) and with 5 % of MBAAm ($\blacksquare$, $\square$), at 25 ºC.

Figure 6 shows that the excess of the initiator, used in the pre-gel solution, produce an acidic media inside the gel matrix. When a membrane sample is immersed in a volume of water, fast leaching of hydrogen ions occurs due to a decrease of initiator concentration as well as to the washing of the membrane. This suggests that the hydrolysis of the amide groups of polyacrylamide [35] may occur. Both the processes can justify the decreasing of the distribution coefficients with the increase of electrolyte concentration, as well as the linear variation of the desorption isotherms. As outside electrolyte concentration increases the probability of ion-polymer interactions decreases due to a limited number of sites where these interactions can occur.
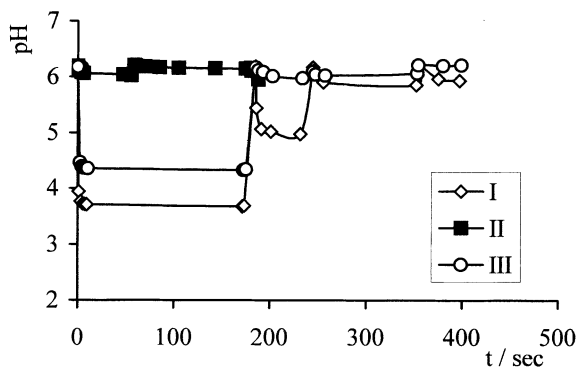

Fig. 6. Effect of leachates of the PAAm in the pH of water as a function of time, at 25 ºC. (I) PAAm, 1% MBAAm, 1% $Na_2S_2O_8$, m(sample)=2.5847 g; (II) PAAm, 1% MBAAm, 0.01% $Na_2S_2O_8$, m(sample)=3.0338 g; (III) PAAm, 1% MBAAm, 0.1% $Na_2S_2O_8$, m(sample)=2.9526 g; The sharp increase on pH means a change of the leachate solution to fresh water.

3.2. Transport properties

Fickian diffusion coefficients, D_F, of KCl and LiCl in polyacrylamides are shown in the Table 2 and Table 3, respectively. The D_F, were computed directly from the flux on the steady-state conditions,

$$D_F = P / K \qquad (9)$$

where K is calculated on the basis of sorption isotherms and P is the permeability coefficient.

The permeability of hydrogel membranes to electrolyte was calculated in assumption of steady-state flux established after some period of non-stationary diffusion. This flux is unaffected by other physical or chemical processes (e.g. ion-ion, ion-water and ion-polymer interactions) completed at an earlier stages. However, another formula normally used in the permeability experiments for calculation of the diffusion coefficients is not applicable in our case. This formula links diffusion coefficient to time-lag of establishment of the steady-state flux. As the time-lag depends on all the above interactions, the apparent diffusion coefficient is too far from its physical meaning. When the experimental data of K were not available, an adjustment equation of the experimental data shown in Figures 4-5 was used. To analyse the effect of the polymeric matrix on the electrolyte mobility as well as to evaluate how the polymer may influence (affect) the electrolyte-water and electrolyte-electrolyte interactions, the D_F were compared with the mutual diffusion coefficients, D_0, of KCl and LiCl in aqueous solutions (Table 2 and Table 3, respectively). These experimental data were calculated using an open-ended conductimetric capillary cell. The D_0 values are a mean of, at least, three different measurements of mutual diffusion coefficients. The experimental mutual diffusion coefficients of LiCl aqueous solutions are lower than those for KCl, as a function of concentration, as we expected. A possible explanation is: due to high charge density of lithium ion, its hydration number is high and consequently the ion Li^+ diffuses slowly with its hydration shells [34]. This is a clear consequence of the weaker interactions K^+-H_2O relatively to Li^+-H_2O. On the other hand, at concentrations higher than 0.3 M, diffusion coefficients increase, especially because of ion-pair formation. We may also observe that there is a higher dependence of diffusion coefficients of KCl on the concentration. This phenomenon can be explained by the viscosity properties of the different solutions. The concentrated LiCl aqueous solutions show a larger increase in viscosity with concentration than KCl [36]. As a consequence, the variation of the diffusion coefficient is a balance of the viscosity effect and ion-pair formation. In the LiCl case the viscosity effect has more influence than in the KCl.

The Fickian diffusion coefficients of the electrolytes are only one order of magnitude lower than in aqueous solutions, and the D_F dependence on electrolyte concentration is similar to that occuring in aqueous solution. In a first approach, the D_F as a function of the electrolyte concentration, C_S, inside gel I, is similar to that in free solution: the D_F(KCl) is higher than D_F(LiCl). The increasing hydration radius of the lithium ions and the decreasing K^+ hydration radius due to the hydrophilic character of the matrix, as pointed out before [6 (pp.96)] can justify this fact. Another evidence is that D_F increases with the electrolyte concentration. This phenomenon may be interpreted as a consequence of electrolyte ion-pair formation [6]. This also suggests that the water inside gel have an important role in the diffusion mechanism in this gel once enhance the ion-ion and ion-water interactions. However, inside gel II D_F(LiCl) > D_F (KCl). The high charge density of lithium may promote the ion-pair formation [37],

predominant when the water concentration decreases and, consequently, the diffusion coefficients increase once, as a rule, the hydrodynamic resistance of the medium to one particle is smaller than the total resistance to solvated ions.

Table 2
Transport coefficients of KCl in polyacrylamides (P and D_F) and in aqueous solutions (D_0), at 25°C

Gel	c_S / M	$P \pm s$ / $/\ (10^{-9}\ m^2\ s^{-1})$	$D_F \pm s$ / $/(10^{-10}\ m^2\ s^{-1})$	$D_0 \pm s$ / $/(10^{-9}\ m^2\ s^{-1})$
I	0.1	1.4 ± 0.4	5.1 ± 1.5	1.853 ± 0.010
	0.2			1.839 ± 0.013
	0.3	1.25 ± 0.06	5.5 ± 0.3	1.832 ± 0.012
	0.5	1.2 ± 0.1	5.8 ± 0.5	1.816 ± 0.011
	0.7	1.3 ± 0.2	6.7 ± 1.0	1.886 ± 0.026
	1.0	1.6 ± 0.2	8.4 ± 1.1	1.936 ± 0.003
	2.0			2.049 ± 0.024
II	0.1	0.8 ± 0.1	2.6 ± 0.3	
	0.3	0.7 ± 0.1	3.2 ± 0.5	
	0.5	0.78 ± 0.06	4.46 ± 0.08	
	0.7	0.60 ± 0.04	5.0 ± 0.4	
	1.0	0.7 ± 0.1	5.7 ± 0.5	

Table 3
Transport coefficients of LiCl in polyacrylamides (P and D_F) and in aqueous solutions (D_0), at 25°C

Gel	c_S / M	$P \pm s$ / $/\ (10^{-9}\ m^2\ s^{-1})$	$D_F \pm s$ / $/(10^{-10}\ m^2\ s^{-1})$	$D_0 \pm s$ / $/(10^{-9}\ m^2\ s^{-1})$
I	0.1	9.5 ± 0.2	3.65 ± 0.08	1.294 ± 0.003
	0.2			1.288 ± 0.007
	0.3	8.0 ± 0.6	5.1 ± 0.4	1.285 ± 0.009
	0.5	8.0 ± 0.6	5.6 ± 0.4	1.310 ± 0.002
	0.7	8.55 ± 0.01	6.5 ± 0.1	1.312 ± 0.016
	1.0	9.0 ± 0.6	7.2 ± 1.3	1.322 ± 0.007
II	0.1	6.9 ± 0.2	3.6 ± 0.1	
	0.3	10 ± 1	6.3 ± 0.6	
	0.5	9.2 ± 0.6	6.6 ± 0.4	
	0.7	8.9 ± 0.1	7.2 ± 0.1	
	1.0	10.0 ± 0.3	7.7 ± 0.3	

Once the diffusion of these electrolytes in the polyacrylamides seems to be controlled by the properties of the aqueous solutions, an attempt to justify such variation (D_F *versus* C_S) on the basis of the free volume model [38-39] was made. This model has been largely used to explain the experimental diffusion coefficients of solutes in the homogeneous hydrogels. In the free volume model the diffusion coefficients of the solute, in aqueous solution, inside polymer can be expressed as

$$D_F / D_0 = k_1 \exp (-k_2 \, r_S{}^2 \, \varphi / (1 - \varphi)] \qquad (10)$$

respectively, where φ is the polymer volume fraction and r_s is the solute radius. k_c, k_1 and k_2 are some undefined structural constants. The polymer volume fraction was calculated from eq. (11) [19], assuming in the swelling process that polymer density, ρ, does not suffer alterations and all sorbed electrolyte has a density, d, similar to that in aqueous solution.

$$\varphi = \{1 + [(Q - 1) \, \rho / d]\}^{-1} \qquad (11)$$

Figures 7 and 8 show reasonable fitting of the experimental data with eq. (10). Parameters involved in this equation were deduced using linear regression $\ln (D_F / D_0)$ vs $[\varphi / (1 - \varphi)]$, and the results of this treatment are reported in Table 4.
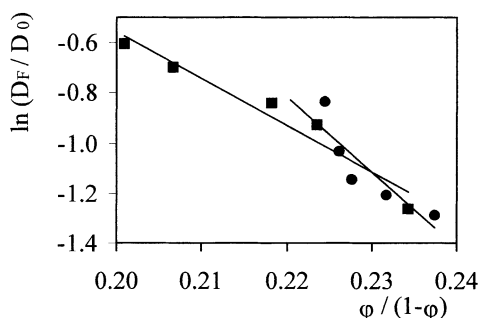

Fig. 7. Application of the free volume model, eq. (12), to the Fickian diffusion coefficients of KCl ($\bullet$) and LiCl ($\blacksquare$), in function of polymer volume fraction of PAAm with 1 % of cross-linker.
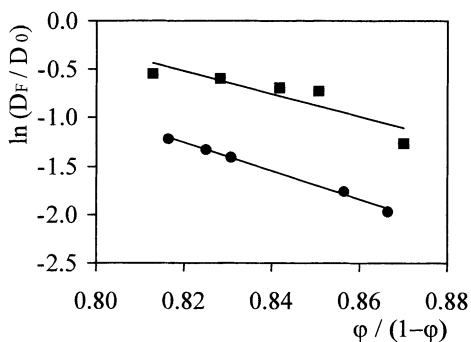
Fig. 8. Application of the free volume model, eq. (12), to the Fickian diffusion coefficients of KCl ($\bullet$) and LiCl ($\blacksquare$), in function of polymer volume fraction of PAAm with 5 % of cross-linker.

The dependence of electrolyte diffusion coefficient on water concentration in polymer matrix can be expected, whereas explanation of values shown in Table 4 requires further discussion.

The eq. (10) introduces a parameter – the solute radius (r_S)- that deserves a detailed analysis, especially because we are talking about concentrated electrolyte aqueous solutions. The diffusing media is clearly aqueous. For this reason ion-ion, ion-water and water-water interactions, as pointed out before, may have significant contributions to the diffusion mechanism. As a consequence, although the electrolyte may be assumed as an independent kinetic body (hydrated), an experimental difficulty arises with respect to determination of the r_S. This comes from the fact that the mean distance of approach of the ions, a, depends on the concentration [34, 40]. The value of a can change from the sum of the hydrated ion radii to a limit value equal to the sum of crystallographic radii, when the ions collapse forming an ion-pair. If this dependence is of complicated nature, and its computation a difficult task, in aqueous electrolyte solutions [e.g. 15, 37], all these difficulties are enhanced when we have more complicated systems, as those described in this paper. An a dependence on the electrolyte concentration, in a system containing an ion (K^+) which produces a break-effect on the water structure, inside a very hydrophilic media (gel I), may justify the poor correlation between the experimental data and the eq. (9).

Table 4
Regression results of application of Free Volume Model, eq. (12), to electrolyte diffusion in hydrogels with different percentage of cross-linking

Gel	electrolyte	r_S* / Å	$\ln(k_1)$	k_2	R^2
I	KCl	3.8	5.8	2.1	0.77
II	KCl	3.8	11	1.0	0.99
I	LiCl	4.25	3.2	1.0	0.95
II	LiCl	4.25	9.3	0.7	0.79

* The values of r_S are the values of the minimum mean distance of approach of the ions [25].

This dependence decreases with more charge density ions, Li^+, and more cross-linked polymers [6 (pp. 96)]. Once the size of the hydrated LiCl species is larger than the KCl species, it seems reliable that an increase in the cross-linker concentration makes difficult the diffusivity of such species. As a consequence the diffusing entities will tend to diffuse decreasing the mean distance of approach of the ions and therefore the dependence of a on concentration becomes more relevant.

The k_2 values show also that the diffusion of KCl is more dependent on the water concentration than the LiCl. This should be expected, if we take into account the structure-break effect of the K^+ ions (and also Cl^-) on the water structure. Therefore, the polymer-solvent interactions, or even the possible ion-polymer interactions, are more important in the KCl systems, and decrease with the increase of cross-linker. As a consequence we may point out that the electrolyte diffusion is not dependent on the macromolecular structure itself but on the hydrated macromolecular structure.

The k_1 values show that the screening sieving effect of the matrix on the electrolyte diffusion can not be neglected. However, the k_1 values seem to be anomalous once they are higher than the unity. However, if we compare the diffusion coefficients of the electrolytes, inside hydrogels and in free solution (D_F and D_0, respectively), as a function of the

concentration (C_S and c, respectively), Figure 9, we find a similar behaviour of the electrolytes in the different systems: the diffusion coefficients are virtually linear with the concentration and their slope are of the same order of magnitude; the Fickian diffusion coefficients of LiCl are similar in both gels and although the D_F of KCl are higher in the gel I, the $D_F(C_S)$ dependence is stronger in the gel II.
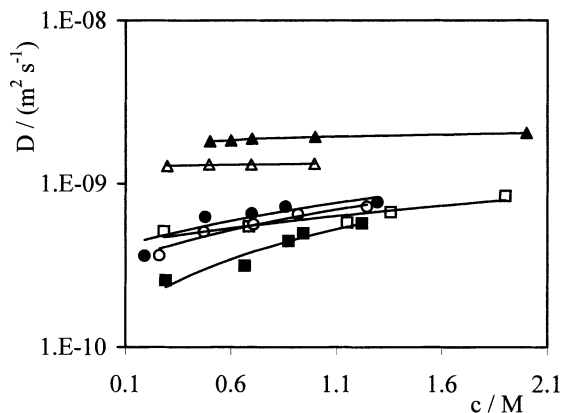

Fig. 9. Comparison between the diffusion coefficients, D, of the KCl (bold points) and LiCl (white points) in aqueous solutions (Δ, $\blacktriangle$) and inside polyacrylamides (gel I - $\bullet$, $\circ$; gel II - $\blacksquare$, $\square$) as function of the concentration, c.

4. CONCLUSIONS

Strong electrolytes (KCl and LiCl) show an interesting behaviour inside polyacrylamides with different degrees of cross-linking. The water content controls the diffusion process. The difference observed in the diffusion of LiCl and KCl may be explained taking into account the ion-ion, ion-water, and water-polymer interactions accompanying the diffusion. The role of these is determined by the thermodynamic features of the cations as well as by the degree of cross-linking (water concentration).

An attempt to explain such experimental data quantitatively was made on the basis of the free volume theory. However some limitations related to the specific character of the electrolyte solutions, show that some work must be done in order to find a more feasible explanation of the experimental data reported in this work.

REFERENCES
1. B. Ramaraj and G. Radhakrishnan, J. Appl. Polym. Sci., 51 (1994) 979.
2. D.G. Pedley, P.J. Skelly and B. Tighe, Br. Polym. J., 12 (1980) 99.
3. K.S. Kazanskii and S.A. Dubrovskii, Adv. Polym. Sci., 104 (1992) 97.
4. M.M. Araújo and J.A. Teixeira, Int. Biodeter. Biodegradat., 40 (1997) 63.
5. T. Tanaka, Encyl. Polym. Sci. Eng., 6 (1986) 514.
6. G.E. Zaikov, A.L. Iordanskii, V.S. Markin, Diffusion of Electrolytes in Polymers, VSP, Utrecht, 1988.

7. V.M.M. Lobo and A.J.M. Valente, Polym. Degrad. Stab., 44 (1994) 147; A.J.M. Valente, A.Ya. Polishchuk, V.M.M. Lobo, H.D. Burrows, Langmuir, 16 (2000) 6475.

8. Y. Saito, H. Kataoka, T. Sakai and S. Deki, Electrochimica Acta, 46 (2000) 1747.

9. J.S. Mackie and P. Meares, Proc. Royal Society, Ser. A, 232 (1955) 498; J.S. Mackie and P. Meares, Proc. Royal Society, Ser. A, 232 (1955) 510.

10. M. Kremer, E. Pothmann, T. Rossler, J. Baker, A. Yee, H. Blanch and J.M. Prausnitz, Macromolecules, 27 (1994) 2965.

11. B. Amsden, Macromolecules, 31 (1998) 8382.

12. A.Ya. Polishchuk, G.E. Zaikov, Multicomponent Transport in Polymer Systems for Controlled Release, Gordon Breach Sci. Publ. Amsterdam, 1997.

13. A.Ya. Polishchuk, L.A. Zimina, N.N. Madyuskin, G.E. Zaikov, Polym. Sci., 35 (1993) 80.

14. O.Ya. Samoilov, Discuss. Faraday Soc., 24 (1957) 141.

15. V.M.M. Lobo, Pure Appl. Chem., 65 (1993) 2613.

16. P. Turq, J. Barthel, M. Chemla, Transport, Relaxation, and Kinetic Processes in Electrolyte Solutions, Springer-Verlag, Berlin, 1992.

17. H.Yasuda, C.E. Lamaze, L.D. Ikenberry, Makromol. Chem., 118 (1968) 19.

18. C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, New York, 1953.

19. H.J. Naghash and O. Okay, J. Appl. Polym. Sci., 60 (1996) 971.

20. J.N. Agar and V.M.M. Lobo, J. Chem. Soc. Faraday Trans., 71 (1975) 1659.

21. V.M.M. Lobo and A.J.M. Valente, Port. Electrochim. Acta, 14 (1996) 133.

22. V.M.M. Lobo, D.B. Murtinho, M.H. Gil, F.P. Garcia and A.J.M. Valente, Intern. J. Polymeric Mater., 33 (1996) 221.

23. V.M.M. Lobo and M.H.S.F. Teixeira, Electrochim. Acta, 254 (1979) 565.

24. A.C.F. Ribeiro, V.M.M.Lobo and J.J.S. Natividade, J. Mol. Liquids. Accepted for publication.

25. V.M.M.Lobo, A.C.F. Ribeiro and S.G.C.S. Andrade, Ber. Buns. Phys. Chem., 99 (1995) 713.

26. V.M.M. Lobo, A.C.F. Ribeiro and L.M. Verissimo, J. Chem. Eng. Data, 39 (1994) 726.

27. V. Vitagliano, Gazz. Chim. Ital., 90 (1960) 876.

28. J.A. Rard and D.G. Miller, J. Sol. Chem., 12 (1983) 413.

29. J.O.'M. Bockris, A.K.N. Reddy, Modern Electrochemistry, 6th ed., Plenum Press, New York, 1970.

30. J.P. Baker, D.R. Stephens, H.W. Blanch and J.M. Prausnitz, Macromolecules, 25 (1992) 1955.

31. S. Saito, J. Polym. Sci. (A-1), 7 (1969) 1789.

32. J.-M. Corpart and F. Candau, Macromolecules, 26 (1993) 1333.

33. F. Candau and J.F. Joanny, Polyampholytes, in J.C. Salamone (Ed.), Polymeric Materials Enc., CRC Press Inc., Florida, 1996. Vol. 7, pp. 5476-5488.

34. R.A. Robinson and R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworths, London, 1959.

35. M. Ilavski, J. Hrouz, J. Stegskal and K. Bouchal, Macromolecules, 17 (1984) 2868.

36. V.M.M. Lobo, Handbook of Electrolyte Solutions, Elsevier Sci. Publ, Amsterdam, 1990.

37. L. De Mayer and G. Kessling, J. Mol. Liquids, 67 (1995) 193.

38. N.A. Peppas, C.T. Reinhart, J. Membr. Sci., 15, (1983) 275.

39. C.T. Reinhart, N.A. Peppas, J. Membr. Sci., 18, (1984) 227.

40. J. Kielland, J. Am. Chem. Soc., 59 (1973) 1675.