

Cu(II)/Cu(0) in the presence of bromazepam follows a similar pattern as discussed, most probably due to the presence of the bipyridyl moiety. Since complex reduction occurs at potentials more positive than the reduction of the 4-5 azometine group of bromazepam, it is not surprising that this redox reaction should not be affected by complex formation.

Acknowledgements: The authors thank Roche Farmacêutica (Lisboa) for the supply of bromazepam. One of us, V.F., thanks financial support from the Associação das Universidades de Língua Portuguesa (AULP).

References

1. W.F.Smyth, "Voltammetric Determination of Molecules of Biological Significances", John Wiley and Sons, Chichester 1992.
2. M.R.Smyth, T.S.Beng, W.F.Smyth, *Anal.Chim.Acta*, 92 (1977) 129.
3. W.F.Smyth, R.Scannell, T.K.Goggih, D.Lucas-Hernandez, *Anal.Chim.Acta*, 141 (1982) 321.
4. J. Hernandez-Mendez, C.Gonzales-Perez, M.I.Gonzalez-Martin, *Anal.Chim.Acta*, 153 (1983) 331.
5. S. M.Sultan, F.E.Q.Suliman, *Analyst*, 121 (1996) 617.
6. A.M.Mota, M.M.Correia dos Santos, "Trace Metal Speciation of Labile Chemical Species in Natural Waters: Electrochemical Methods" in D. Turner and A.Tessier(eds) "Metal Speciation and Bioavailability", ch.5, p.202, John Wiley and Sons, Chichester 1995.
7. M.L.Simões Gonçalves, L.Sigg, *Electroanalysis*, 3(1991)553.
8. A.J.Bard, L.R.Faulkner, "Electrochemical Methods, Fundamentals and Applications", ch.5, John Wiley and Sons, New York 1980.
9. J.Heyrovsky and J.Kuta, "Principles of Polarography", Publishing House of the Czechoslovak Academy of Sciences, Prague 1965.
10. N.E.Schmith, J.H.Pan, R.H.Philp, Jr, *J.Electroanal. Chem.*, 241 (1988) 281.
11. M.M.Correia dos Santos, M.L.Simões Gonçalves, *Electroanalysis*, 3 (1991) 131.
12. M.M.Correia dos Santos, C.M.L.Freire Lopes, M.L.Simões Gonçalves, *Bioelectrochem. Bioenerg.*, 39 (1996) 55.
13. M.M.Correia dos Santos, P.M.P.Sousa, A.M.M.Modesto, M.L. Simões Gonçalves, *Bioelectrochem. Bioenerg.*, 45 (1998) 267.

Received, June 14, 1999
Revised, July 30, 1999

DIFFUSIVITY OF NON-ASSOCIATED ELECTROLYTES IN ACRYLAMIDE-BASED HYDROGELS COUPLED WITH A CAPILLARY CELL

Artur J.M. Valente, Victor M.M. Lobo^{#*} and Alexandre Ya. Polishchuk[&]
Department of Management and Industrial Engineering, Lusiada University, 4760 V.N. Famalicão, Portugal;
avalente@ave.fam.ulusiada.pt
[#]*Department of Chemistry, University of Coimbra, 3049 Coimbra, Portugal; vlobo@ci.uc.pt*
[&]*Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin Street, Moscow 117334, Russia*
chembio@sky.chph.ras.ru

Abstract

A technique has been developed to measure the overall diffusion coefficients of KCl and LiCl in acrylamide hydrogels immersed in electrolyte solutions. Once a majority of these kind of polymers are used in connection with electrolyte aqueous solutions, this technique allows the determination of diffusion coefficients representative of systems of aqueous electrolyte solutions normally surrounding polymeric materials. The capillary cell is based on the open-ended capillary conductimetric cell earlier designed to measure diffusion coefficients of electrolytes in aqueous solutions. Polymeric matrices of different hydrophilic character have been studied showing the complex interactions between the different species (water with different structures, polymer and electrolyte). The different thermodynamic effects of cations on the water structure enhance this behaviour. The water structure breaking effect due to potassium ions, when compared with lithium ions, results in the diffusion flux decrease, mainly due to the decrease of water content available as diffusional media inside the matrix.

Keywords

Electrolyte, Diffusion Coefficients, Hydrogels

Introduction

The hydrogels are materials with applications in many fields, such as bio-separation [1] and wastewater treatment [2] among others. In a great number of those applications the hydrogels are in contact with electrolyte solutions. This is the main reason initiating our study of electrolyte behaviour in a hydrogel matrix immersed in aqueous electrolyte solutions.

In a polymer network, water normally exists in a continuum of states between two extremes [3]. They are: water molecules strongly associated with the polymer network through hydrogen bonding (so-called non-freezing water) and much more mobile water molecules unaffected by the polymeric environment (freezing water). However, there is no much information about the electrolyte effect on that water and polymer structure. This results from the assumption that, in the

highly hydrophilic neutral gel networks, the system electrolyte-water-gel can be considered as an aqueous system. In our recent paper [4] we concluded that the electrolyte diffusion mechanism in different hydrogels is clearly non-Fickian. This behaviour can be justified by the interactions of the components of the system as for example water-water interactions of different types. The effect of other properties, as for example, the possible occurrence of hydrolysis as well as the swelling processes, can not also be neglected. For this reason we are interested in describing the electrolyte diffusion process using a more accurate physical parameter. In this paper we present LiCl and KCl diffusion coefficients in different hydrogels derived from acrylamide with different hydrophilicity degrees. The water sorbed by the gel network is quantitatively represented by the water gain (H_p), the ratio of the weight of water in the hydrogel to the weight of dry gel, expressed as a percentage:

$$H_p = (\text{weight of gel in water} - \text{weight of dry gel}) * 100 / \text{weight of dry gel} \quad (1)$$

This knowledge will help us to know how to change the macromolecular structure as well as how the electrolyte influences the hydrogel features and its functionality.

Experimental

Reagents and Solutions

0.1 M to 1.0 M solutions of KCl (Riedel-de Häen, *pro analysis*) and LiCl (Riedel-de Häen, *pro analysis*) were prepared directly from the salts previously dried [5] at 110 °C and 180 °C until constant weight, respectively. Degassed distilled water was used.

Acrylamide (2.5 M in tri-distilled water), methyl methacrylate (2.5 M in 2-propanol) and 2-propanol were from Riedel-de Häen. N,N'-methylene-bis-acrylamide (MBAAm) was from Merck, sodium persulphate from Fluka AG, and poly(vinyl alcohol) (PVA) of molecular weight of 13000 - 23000 from Aldrich Co. All reagents were of *pro-analysis* quality and were used as received. Tri-distilled water was used. All experiments were carried out at 25 °C.

Synthesis

Acrylamide-based hydrogels were prepared by free-radical co-polymerisation of acrylamide (AAm) and methylmethacrylate (MMA), using MBAAm as cross-linking agent. The $\text{Na}_2\text{S}_2\text{O}_8$ was used to initiate the polymerisation; the initiator concentration was held at a constant value of 1 % (weight/volume) for all synthesis.

The membranes were prepared polymerising the pre-gel solution inside two glass sheets separated by plastic rubber gasket. Spring clips were used to hold the glass sheets together. After

* To whom correspondence should be addressed.

this procedure, the mould was placed in the oven at 50 °C for approximately 2 hours. The hydrogel membranes were then removed from the mould, and they are stored in an exsiccator at about 100 % humidity. The composition of the pre-gel solutions is shown in table 1.

Table 1 - Composition of pre-gel solutions.

Hydrogel	Monomers	V(AAm) / V(MMA)	[MBAAm] / % (w/v)
I	AAm	1	1
II	AAm	1	5
III	AAm + MMA	4 / 1	5
IV	AAm + MMA	3 / 2	5

The poly(vinyl alcohol), in the concentration of 0.05 - 0.1 % (w/v), was used in the gel IV to increase the mechanical strength and so to be handled without breaking.

The Modified Open-Ended Conductimetric Capillary Cell

The conductimetric cell technique is based in the open-ended capillary cell [6, 7]. However, the need for measuring diffusion in polymeric matrices required some design alterations [8]. Basically, the technique consists of two capillaries positioned in the same axis and at the same distance of a central electrode. Platinum electrodes close one end of each tube. These electrodes as well as the central electrode enable us to measure the electrical resistance variation with time. The upper and lower tubes are filled with electrolyte solutions $0.5 c_b$ (top solution) and $1.5 c_b$ (bottom solution), where c_b is the bulk solution concentration. The membranes previously immersed in the top and bottom solutions are positioned in the open-end of the capillary cell, as schematic represented in figure 1, with the help of a screw. This procedure is done with all precautions in order to be sure that there is no damage on the membranes as well as to guarantee a hermetically interface between the membrane and the capillaries.

Finally the cell is immersed in the bulk solution and the time is recorded.

The electrolyte flux is measured through the electrical resistance ratio (W) of top electrode (R') and bottom electrode (R'') as function of time (t).

$$W = R' / R'' \quad (2)$$

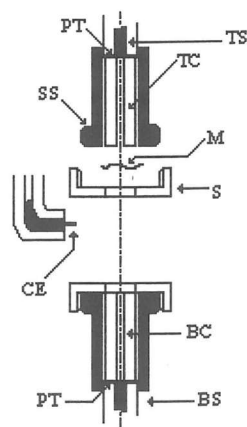


Figure 1 - Schematic representation of the modified open-ended conductimetric cell. TS, BS = support capillaries; TC, BC = top and bottom diffusion capillaries; S = screw and membrane support; SS = screw support; M = membrane; CE = central electrode; PT = platinum electrodes.

The electrical resistances R' and R'' are dependent of three different electrical resistance components (eq. 3): the electrical resistance of electrolyte inside capillary (R_1), the electrical resistance of the polymeric matrix (R_2), and the electrical resistance of bulk solution between central electrode and the matrix surface (r). For simplicity we will use the top capillary as example (figure 2).

$$R' = r + R_1 + R_2 \quad (3)$$

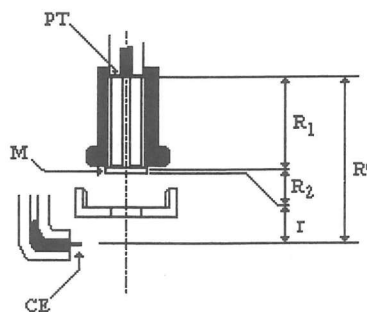


Figure 2 - Electrical resistance components in the top part of the conductimetric cell (the same is valid to the bottom part of the cell). PT = platinum electrode; M = polymeric membrane; CE = central electrode; R_1 = electrical resistance of electrolyte solution inside capillary; R_2 = electrical resistance of the polymeric membrane; r = electrical resistance of bulk electrolyte solution; $R' = R_1 + R_2 + r$.

However the technical design does not permit an independent measure of the electrical resistances (R_1 and R_2). Therefore an alteration in the electrical resistance, for example, $\Delta R'$, is a measure of the electrical resistance changing in capillary and in membrane all together:

$$\Delta R' = r + \Delta (R_1 + R_2) \quad (4)$$

For such task we can describe the diffusion process in the capillary and in the polymer using Fick's 2nd law:

$$\partial C / \partial t = \partial / \partial x (D \partial C / \partial x) \quad (5)$$

where C is an average concentration of the electrolyte inside capillary and membrane, D is the diffusion coefficient of the electrolyte considering the diffusion path of the polymer and capillary, t is the time and x is the spatial co-ordinate of an axis where the diffusion proceeds.

Establishing the following boundary and initial conditions

$$\partial C / \partial x = 0 \text{ at } x = 0 \text{ (at the top of the top capillary or at the bottom of bottom capillary)} \quad (6)$$

$$C = Kc_b; \text{ at } x = d \text{ (the polymer/bulk interface)}$$

$$C = C_0 \text{ at } t = 0$$

we can solve equation (5) using [9]

$$C = \sum_{n=0}^{\infty} (-1)^n [4(C_0 - c_{\infty}) / \pi(2n+1)] \exp[-\pi^2(2n+1)^2 D t / 4 d^2] \cos(\pi(2n+1) x / 2d) + c_{\infty} \quad (7)$$

where d is the sum of the capillary length (a) plus the membrane thickness (l), C_0 is the electrolyte initial average concentration inside the capillary and the membrane, K is the distribution coefficient between aqueous solution and polymer, and c_{∞} is the electrolyte average concentration inside the capillary and the membrane at equilibrium: $c_{\infty} = c_b(a + Kl) / d$.

Taking the specific resistance in the capillary and in the membrane as equal [8], and using equations (2), (3) and (7) we find [7]

$$\ln (Y_t - Y_{inf}) = k - \lambda t \quad (8)$$

where k is a constant. Y_t is described as

$$Y_i = 10^4 / (1 + W) \tag{9}$$

and Y_{inf} is the value of Y_i when the concentration gradient tends to zero, and λ is defined as

$$\lambda = \pi^2 D / 4 d^2 \tag{10}$$

Results and Discussion

Table 2 shows some physical features of the hydrogels when in equilibrium with water. The different gels show different hydrophilicity degrees, which decrease with an increase of MBAAM and/or methyl methacrylate content. The addition of the co-monomer MMA to acrylamide results in an increase of the mechanical strength as well as in the rigidity of the membranes (the polymer density increases). In fact whilst gels I and II show a swelling process when immersed in water, in gels III and IV this behaviour does not occur. This explains the different variation of the water concentration in the membranes (C_{wco}).

Table 3 shows the diffusion coefficients (D) of KCl and LiCl in hydrogel/capillary systems (gels I to IV). These results show a very good precision, although lower than that obtained for the diffusion coefficients of the electrolyte in free solution [11]. This decreasing in precision can be explained as follows: the diffusion coefficients measured with the conductimetric cell correspond to a weighted average from the electrolyte sorption and desorption kinetics which undergoes at the top and bottom matrices, respectively. However these kinetics are not necessarily the same [12] and can be dependent on the matrix and electrolyte concentration C , which is not accurately controlled.

Table 2 – Some physical features of the hydrogels in equilibrium with water, at 25 °C.

Hydrogel	H_p / %	d_p / (g cm ⁻³)	C_{wco} / (w/w)
I	1060	0.36	0.921
II	476	0.24	0.826
III	412	0.65	0.809
IV	204	0.64	0.679

H_p = water gain; d_p = polymer density; C_{wco} = water concentration in gel at equilibrium.

Table 3 – Diffusion coefficients (D) of KCl and LiCl in different hydrogel/electrolyte systems.

hydrogel	[salt] / M	D (KCl) $\pm s$ / (10 ⁻¹⁰ m ² s ⁻¹)	D (LiCl) $\pm s$ / (10 ⁻¹⁰ m ² s ⁻¹)
I	0.1	6.1 \pm 0.5	8.3 \pm 0.1
	0.3	7.5 \pm 2.0	9.4 \pm 0.8
	0.5	7.2 \pm 0.9	10.1 \pm 0.1
	0.7	6.5 \pm 0.7	10.1 \pm 0.1
	1.0	7.6 \pm 0.3	10.1 \pm 0.1
II	0.1	4.4 \pm 1.0	6.8 \pm 0.6
	0.3	6.4 \pm 1.0	8.3 \pm 0.6
	0.5	8.2 \pm 0.9	8.6 \pm 0.3
	0.7	8.1 \pm 0.2	8.5 \pm 0.2
	1.0	8.3 \pm 0.1	9.5 \pm 0.2
III	0.1	7.1 \pm 0.7	8.3 \pm 0.2
	0.3	8.7 \pm 0.4	8.3 \pm 0.6
	0.5	9.3 \pm 1.2	7.5 \pm 0.1
	0.7	9.2 \pm 0.2	5.8 \pm 0.0
	1.0	9.8 \pm 0.4	6.8 \pm 0.1
IV	0.1	6.1 \pm 0.3	6.1 \pm 0.1
	0.3	4.6 \pm 0.4	5.0 \pm 0.6
	0.5	4.6 \pm 0.5	6.0 \pm 0.8
	0.7	4.4 \pm 0.2	6.3 \pm 0.1
	1.0	4.4 \pm 0.0	6.4 \pm 0.1

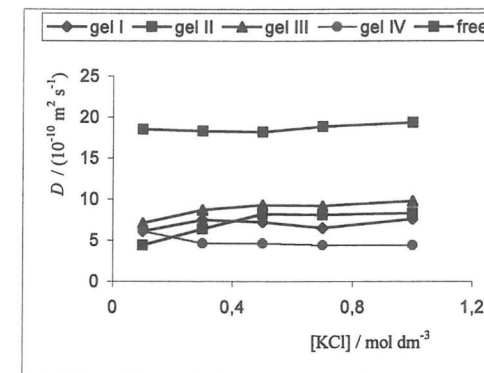


Figure 4 – Diffusion coefficients, D , of KCl in hydrogel/KCl systems and in free solution.

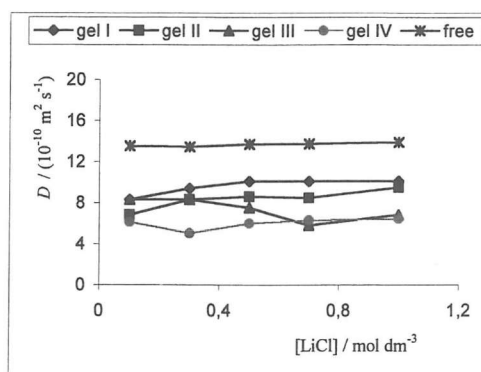


Figure 5 – Diffusion coefficients, D of LiCl in hydrogel/LiCl systems and in free solution.

From table 3 and figures 4 and 5 we conclude that for each hydrogel the diffusivity of electrolytes almost does not change with concentration (within the experimental error) indicating the thermodynamic character of the measurable parameter. However, the exceptions do not have any meaning when compared with those obtained through the Fickian diffusion coefficients of similar systems [4].

Except for gel III, the diffusion coefficients of LiCl are higher than those of KCl. This behaviour shows an anomalous diffusion process of KCl especially inside the more hydrophilic hydrogels with a great content of water. A possible explanation can be found in the effect of the cations on the water structure. The water molecules inside hydrogels I and II are very stable due to interaction water-polymer as well as water-water. When the KCl flows through gel, and due to the water structure-breaking of potassium ions, the water molecules of the K^+ hydration shells tend to interact with the gel water molecules in order to find a less energetic state. This increase in water-water interactions will tend to decrease the diffusing process which is not accompanied by the lithium ions once these show opposite features on the water molecule structure due to its high charge density.

Gel III shows a matrix which is the closest to the aqueous system. Methylmethacrylate is responsible for such behaviour. In fact, the amount of such monomer is not large enough to predominate the hydrophobic part in the macromolecular structure as in gel IV, but it is enough to decrease the acrylamide effect on the water structure. The methylmethacrylate increases the hydrophobicity of the hydrogel and renders more difficult the acrylamide-water interactions by steric hindrance [13].

On the other hand, it seems that the electrolyte diffusion process inside gel IV is controlled by the crystallographic radius instead of the hydration radius. This explanation is valid using the arguments cited before.

All these explanations based on the different cation effect on water structure agree with the comparison between diffusion coefficients in hydrogel/capillary system and in aqueous solution (figures 4 and 5). When the different interactions water-water are stronger, the difference between such parameters is also higher. Therefore the high stability of water molecules in the lithium hydration shells may be the cause of a diffusion process similar to that which occurs in aqueous solution.

The influence of water-water interaction on the diffusion process is also supported by water diffusion coefficients of water inside hydrogels, one order of magnitude lower than the water self-diffusion coefficient [10, 14]. In any case we cannot also neglect the possible stronger ion-polymer interaction which arises from the possible hydrolysis of amide groups of acrylamide [15].

References

1. A.E. Ivanov, V.V. Saburov and V.P. Zubov, *Adv. Polym. Sci.* **104** (1992) 135.
2. M.M. Araújo and J.A. Teixeira, *Int. Biodet. Biodeg.* **40** (1997) 63.
3. P.H. Corkhill, A.M. Jolly, C.O. Ng and B.J. Tighe, *Polymer* **28** (1987) 1758.
4. V.M.M. Lobo, A.J.M. Valente, A.Ya. Polishchuk and G. Geuskens. Submitted for publication.
5. C. Duval, "Inorganic Thermogravimetric Analysis", Elsevier, New York, 1953.
6. V.M.M. Lobo, "Diffusion and Thermal Diffusion in Solutions of Electrolytes", Ph.D. Thesis, Cambridge (UK), 1971.
7. J.N. Agar and V.M.M. Lobo, *J. Chem. Soc., Faraday Trans. I* **71** (1975) 1659.
8. V.M.M. Lobo, D.B. Murinho, M.H. Gil, F.P. Garcia and A.J.M. Valente, *Int. J. Polym. Mater.* **32** (1996) 221.
9. J. Crank, "The Mathematics of Diffusion", Oxford Univ. Press, Oxford, 1956.
10. A.J.M. Valente, "Difusão de Electrólitos em Solução Aquosa e em Hidrogéis com Diferentes Graus de Hidrofilicidade", Ph.D. Thesis, Coimbra, 1998.
11. V.M.M. Lobo and A.J.M. Valente, *Port. Electroch. Acta* **14** (1996) 133.
12. A.Ya. Polishchuk and G.E. Zaikov, "Multicomponent Transport in Polymer Systems for Controlled Release", Gordon and Breach Sci. Publ., Amsterdam, 1997.
13. P.H. Corkhill, A.M. Jolly, C.O. Ng and B.J. Tighe, *Polymer* **28** (1987) 1758.
14. R. Mills, *J. Phys. Chem.* **77** (1973) 685.
15. M. Ilavski, J. Hrouz, J. Stegskál and K. Bouchal, *Macromolecules* **17** (1984) 2868.