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Full Length Research Paper

Evaluating the absorption coefficient of NaCl in hydrogels acrylamide

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In this study, acrylamide hydrogels with different amounts of water in the initial reaction mixture were synthesized. NaCl absorption capacity was determined by the hydrogels. It was found that the acrylamide hydrogels are nonselective absorption of chlorine ions or sodium. However, similar solute concentrations inside and outside of the hydrogel were obtained. The diffusion coefficients were determined when the hydrogels were placed in bidistilled water and in aqueous solutions at 50 and 100% saturation.

Key words: Diffusion coefficient, NaCl, acrylamide, hydrogels.

INTRODUCTION

The physical properties of hydrogels in the swollen state are related to the degree and nature of cross-linking, the type and combination of monomers used, and the tactility and crystalline of the polymer that forms the network. The properties of hydrogels enable their use in different fields and in numerous applications (Ratner, 1996; Rojas de Gáscue et al., 2010; Dai et al., 2006;Fundueanuet al., 2009; Sudipto et al., 2002). Consequently, modifying the ability to absorb solutes, the rate of absorption and release of ions, as well as increase the selectivity of absorption of ions by hydrogels, opens an important field to improve the properties and applications of these materials. The composition of the solvent used in the pre-gel solution is an important factor that determines the final properties of the hydrogel (Matzelle et al., 2003; Cortes Ortega, 2013). The ability of hydrogels to absorb water depends on the temperature, pH of the medium and the concentration of salts in the solution (Aouadal et al., 2008; Rojas et al., 2011; Richard et al., 2000). Measuring the ability of hydrogels to absorb water is important for its applications. However, it is important to control the water absorbing capacity of these materials as the higher the water content, the more the biocompatible materials that they have. The purpose of this work is to contribute in the prediction and study the ability to absorb water as well as an electrolyte (NaCl). These materials could be used as semi-permeable membranes.

EXPERIMENTAL

Reagents used in the experiments were: Acrylamide (AM, Sigma, 99%), potassium persulfate (KPS) initiator (TCI Tokyo Kasei, 99%), N,N-metilenbisacrilamida cross-linking agent (NMBA, TCI Tokyo Kasei, 99%), water double-distilled and NaCl (Sigma)

Procedure

Solutions were prepared at 5, 10, 15 and 20% of monomers with 1% of crosslinking agent with respect of 1% acrylamide and initiator. Then the samples were placed in test tubes, bubbled with nitrogen for 2 min and sealed, placed in a constant temperature bath at 60°C for

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three hours. Then the tube was broken by removing the gels and placed in a double-distilled water **for** one week to eliminate material that was not added to the network.Changing this water four times every 24 h as shown in previous work,is sufficient to remove the material added to the network.

As soonas the cleaning process wascompleted, the samples were cut into cylinders 2 cm thick and placed to dry at room temperature for two days and then in a vacuum oven at 45°C until constant weight were achieved. To follow the kinetics of swelling, the xerogel (dry hydrogel) was weighed and placed in double-distilled water, the sample was weighed regularly at different times, the medium was withdrawn and the surface was dried with a paper towel and the samples were returned to the environment, this process was repeated until no weight change was observed. The swelling is determined by the equation:

$$H = \frac{\text{swollen mass} - \text{dry mass}}{\text{dry mass}} = \frac{ms - md}{md} \qquad (1)$$

This process is repeated as the samples were immersed in aqueous solutions of NaCl 50 and 100% saturation at 25°C. As the samples reach equilibrium swelling, theywere removed from the medium and placed to dry (following the process described above), with the initial dried weight and dry weight at the end of the experiment, the mass of solute and water absorbed were determined,the selectivity of the absorption of chlorine ions and sodium ions was also determined. The amount of chlorine ions was determined in the residual solution by argentometric method. Also, the total solids content were determined using gravimetric technique.

RESULTS

Swelling kinetics

The solid lines in Figure 1 are model predictions of swelling of the second order, which is commonly used to model the kinetics of swelling (12). This model has the following form:

$$\frac{dW}{dt} = K(W_{\infty} - W)^2 \qquad (2)$$

Where:

$$H = \frac{\text{swollen mass} - \text{dry mass}}{\text{swollen mass}} = \frac{ms - md}{ms} \; (g_{water}/g_{xerogel}) \qquad (3)$$

It being integrated with W = 0 when t = 0 gives:

$$W = \frac{KW_{\infty}^2 t}{1 + KW_{\infty} t} \qquad (4)$$

Combining equations (1) and (3) gives:

$$W = \frac{H}{H+1} \qquad (5)$$

$$W_{\infty} = \frac{H_{\infty}}{H_{\infty}+1} \qquad (6)$$

Combining equations (5) and (6) into (4):

$$\frac{t(H+1)}{H} = \frac{(H_{\infty}+1)^2}{KH_{\infty}^2} + \frac{H_{\infty}+1}{KH_{\infty}} t \qquad (7)$$

By plotting t (H +1) / H vs time gives a straight line where:

The slope is: $$m = \frac{H_{\infty}+1}{KH_{\infty}} \qquad (8)$$

The intercept $$b = \frac{(H_{\infty}+1)^2}{KH_{\infty}^2} \qquad (9)$$

And the value of K can be calculated:

$$K = \frac{(H_{\infty}+1)^2}{bH_{\infty}^2} \qquad (10)$$

Rearranging equation (7) yields:

$$H = \frac{t}{t(m-1)+b} \qquad (11)$$

Figure 1 shows that the mathematical model of second order kinetics fit with good approximation to the experimental data, both the swelling in water and in solution, for the samples placed in both water and saline solutions.

It can be seen that the water absorbing capacity of the samples increases with increasing proportion of water in the initial reaction mixture. Previous research has established that a higher proportion of water in the initial reaction mixture (Escobar et al., 2002; Katime et al., 1996; Nuño-Donlucas et al., 2004) creates more space available to the growing chains that move away from each other, reaching higher average length between physical undercross points, yielding a more flexible and thus greater capacity to absorb water that are not related (Table 1). The same is true both for the absorption of water and solution.

Table 2 shows that the amount of mass of solution absorbed by the sample increases with increasing salt concentration in the solution.

The amount of salt and water that penetrated the hydrogel was determined (by gravimetric method and the

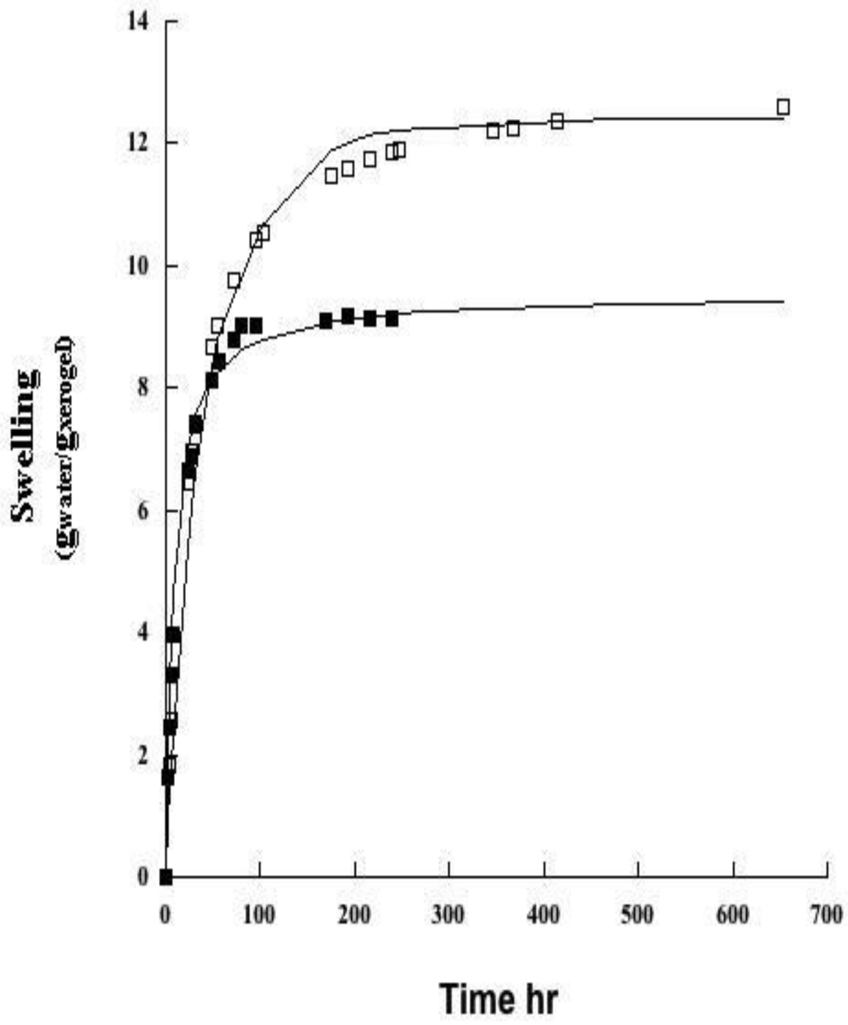

Figure 1. Comparison between the experimental data and the model of t he swelling kinetics, for polyacrylamide hydrogel 20% in water (■) in saline at 100% (□).

Table 1. Acrylamide hydrogels swelling in water or saline solutions.

Acrylamide	20%	15%	10%	5%
W_∞water	9.5278	13.2206	17.0616	41.0029
W_∞ 50% saturation	12.0261	15.6884	21.6883	51.3538
W_∞ 100% saturation	13.0894	17.2957	23.9655	48.9696

Table 2. Amount of water absorbed per gram of xerogel.

	Water $g_{water}/g_{xerogel}$	50% saturacion $g_{water}/g_{xerogel}$	100% saturacion $g_{water}/g_{xerogel}$
20%	9.16	9.86	9.87
15%	12.41	13.15	11.88
10%	16.25	17.81	16.75
5%	38.07	41.06	38.27

Table 3. Solute mass per gram of xerogel and the solute concentration within the hydrogel.

	Solution to 100% of saturation		**Solution to 50% of saturation**	
	$g_{solute}/g_{xerogel}$	**$[Solute]_{hydrogel}$**	**$g_{solute}/g_{xerogel}$**	**$[Solute]_{hydrogel}$**
20%	3.46	25.95%	1.83	15.62%
15%	4.05	25.42%	2.40	15.46%
10%	5.78	25.64%	3.40	16.05%
5%	13.42	25.97%	7.85	16.05%

Figure 2. Physical aspect of hydrogels (90/10) dried before and after to be place in the solution of NaCl, Xerogel (a), 100% saturation (b) and 50% saturation (c).

Table 4. Diffusion coefficients for hydrogels placed in water or saline solutions.

Concentration	**20%**	**15%**	**10%**	**5%**
$D_{water}(cm^2/min)$	2.087E-05	3.248E-05	3.164E-05	1.415E-04
$D_{100\%\ saturation}$ (cm^2/min)	1.241E-05	1.303E-05	1.329E-05	1.376E-05
$D_{50\%\ saturation}(cm^2/min)$	6.181E-06	7.069E-06	7.263E-06	9.983E-06

method argentométrico), and it was found that the salt composition was the same inside and outside (Table 3). Similar results were obtained for the other samples. Also, Table 3 shows the solute absorbed by each sample and the concentration of the solution, though within the hydrogel

With this result, we can establish that the hydrogel does not have selectivity for sodium ions or chloride ions, (it was verified with the analysis of Cl^- in the residual solution (American Society for testing and Materials, 1994; Method 4500 Cl^- B, 1995). Figure 2 shows the NaCl crystals formed after the drying of hydrogels.

Determination of the diffusion coefficient:

$$F_t = \frac{H_t}{H_\infty} = kt^n \tag{12}$$

When applying the Equation (12) for one-dimensional diffusion and plotted (13), as the value of n is close to 0.5, one can establish that the diffusion follows the law of Fick, so it can be applied to the following equation:

$$\ln F_t = \ln\frac{H_t}{H_\infty} = \ln k + n\ln t \tag{13}$$

When the value of n differs from 0.5, then thefollowing equation is applicable:

$$\frac{H_t}{H_\infty} \text{ vs } t^{\frac{1}{2}} \tag{14}$$

Straight line and obtain the diffusion coefficient by (15):

$$\frac{H_t}{H_\infty} = 4\left(\frac{D_w t}{ph^2}\right)^n \tag{15}$$

In this study, it was found that a decrease in the concentration of acrylamide in the pre-gel solution caused an increase in the diffusion coefficient, as it has a network that is more flexible, which means that when you start the process of hydration, water molecules and ions penetrate more easily. In Table 4, it can be seen that the diffusion coefficient of hydrogels in water is higher than the diffusion coefficient obtained when the hydrogels are placed in the salt solutions. The presence of ions in the solution delays the response of the network to hydration. To calculate the value of n was obtained in all cases Using the equation [12]. All diffusion coefficients were calculated using the equation (15), these data were taken from figures A, B and c of appendix

Conclusions

It was found that the water absorbing capacity of the hydrogel depends on the water content in the solution of the pre-gel.In increasing the water content in the solution of the pre-gel and the water absorbing capacity of the hydrogels, it was determined that there is no selectivity in the absorption of chlorine ions or sodium ions by the hydrogels, likewise the reduction in the coefficient of diffusion of the hydrogels was determined as was placed in the salt solutions.However, this study can provide some important parameters for the possible use of these materials as metal ion permeable membranes.

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APPENDIX

Table A. Kinetic parameters for acrylamide hydrogels as a function of the water content in the pre-gel solution determined in double distilled water.

Sample	20%	15%	10%	5%
Slope	1.1050	1.0757	1.0586	1.0244
Intersection (gaguah/ggel)	53.1833	51.6632	30.5606	33.9260
H_∞ (gagua/gxerogel)	9.5278	13.2206	17.0616	41.0029
K(ggel/gaguah)	0.0232	0.0224	0.0444	0.0313
Standard deviation	0.1490	0.1659	0.2952	0.3674

Table B. Kinetic parameters for acrylamide hydrogels as a function of the water content in the pre-gel solution determined in salt solutions at 50% saturation.

Sample	20%	15%	10%	5%
Slope	1.0832	1.0637	1.0461	1.0195
Intersection (gaguamin/ggel)	40.5115	42.5795	31.0550	31.2965
H_∞ (gagua/gxerogel)	12.0261	15.6884	21.6883	51.3538
K (ggel/gaguamin)	0.0297	0.0282	0.0355	0.0341
Standard deviation	0.2660	0.2985	0.4303	1.0844

Table C. Kinetic parameters for acrylamide hydrogels as a function of the water content in the pre-gel solution determined in salt solutions at 100% saturation.

Sample	20%	15%	10%	5%
Slope	1.0764	1.0578	1.0417	1.0204
Intersection (gaguah/ggel)	112.5648	92.9560	71.0982	31.8726
H_∞ (gagua/gxerogel)	13.0894	17.2957	23.9655	48.9696
K (ggel/gaguah)	0.0103	0.0120	0.0153	0.0327
Standard deviation	0.2358	0.2836	0.3587	0.8736

Table D. Diffusion coefficients and parameters of the diffusion equations for hydrogels placed in distilled water.

Concentration	20%	15%	10%	5%
n	0.5577	0.5230	0.5763	0.5912
lnK	-2.1244	-2.0577	-2.1853	-2.6853
R	0.9959	0.9981	0.9975	0.99702
Diffusion coefficients	2.087E-05	3.248E-05	3.164E-05	1.415E-04

Table E. Diffusion coefficients and parameters of the diffusion equations for hydrogels placed in salt solutions at 50% saturation.

Concentration	20%	15%	10%	5%
lnK	-2.2505	-2.2822	-2.3021	-2.6793
R	0.9987	0.9989	0.9999	0.9961
n	0.6036	0.5878	0.5768	0.5372
Diffusion coefficients	6.181E-06	7.069E-06	7.263E-06	9.983E-06

Table F. Diffusion coefficients and parameters of the diffusion equations for hydrogels placed in salt solutions at 100% saturation.

Concentration	20%	15%	10%	5%
lnK	-3.1697	-2.9789	-3.014	-2.8235
R	0.9990	0.9995	0.9994	0.9989
n	0.6874	0.6475	0.6782	0.6030
Diffusion coefficients	1.241E-05	1.303E-05	1.329E-05	1.376E-05

Table G. Concentration of Cl^- in the solution initial and residual.

	Solution to 100% of saturation		Solution to 50% of saturation	
	[Cl] residual	[Cl] initial	$g_{solute}/g_{xerogel}$	$[Solute]_{hydrogel}$
20%	13.545%	15.966%	10.997%	9.194%
15%	15.024%	15.966%	10.434%	9.194%
10%	15.716%	15.966%	9.471%	9.194%
5%	15.504%	15.966%	8.681%	9.194%

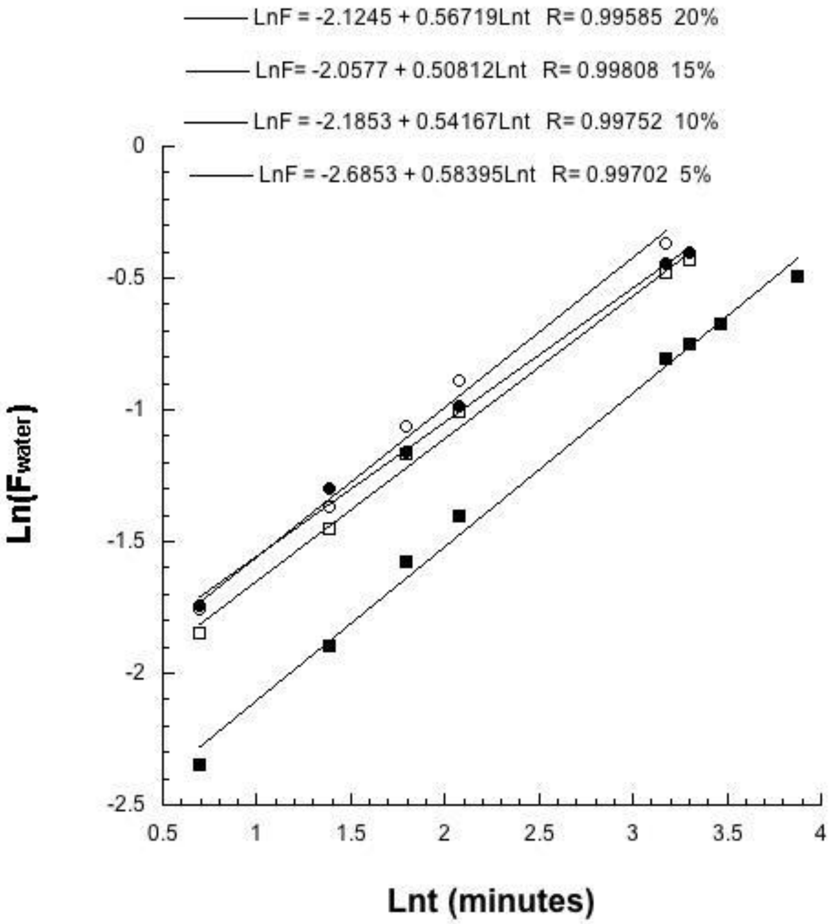

Figure A. Plot equation 12 for determining if the diffusion follows the law of Fick for hidrogeles place in water.

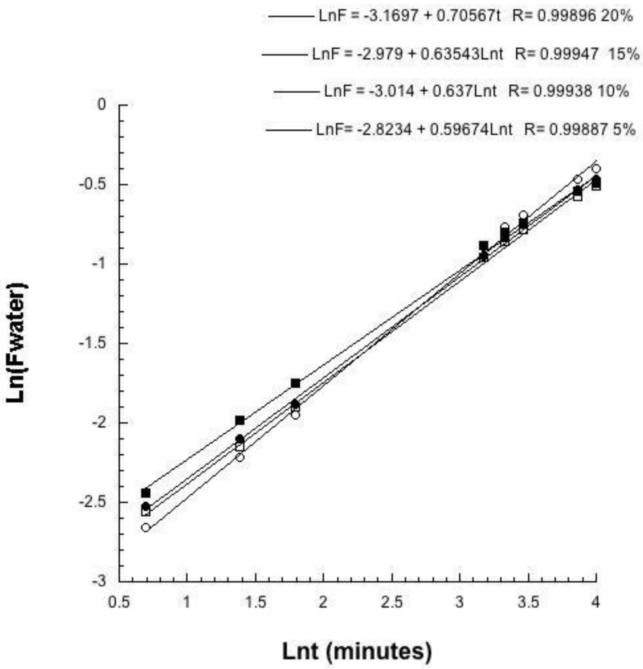

Figure B. Plot equation 12 for determining if the diffusion follows the law of Fick. For hidrogeles place in solution of 100% saturation.

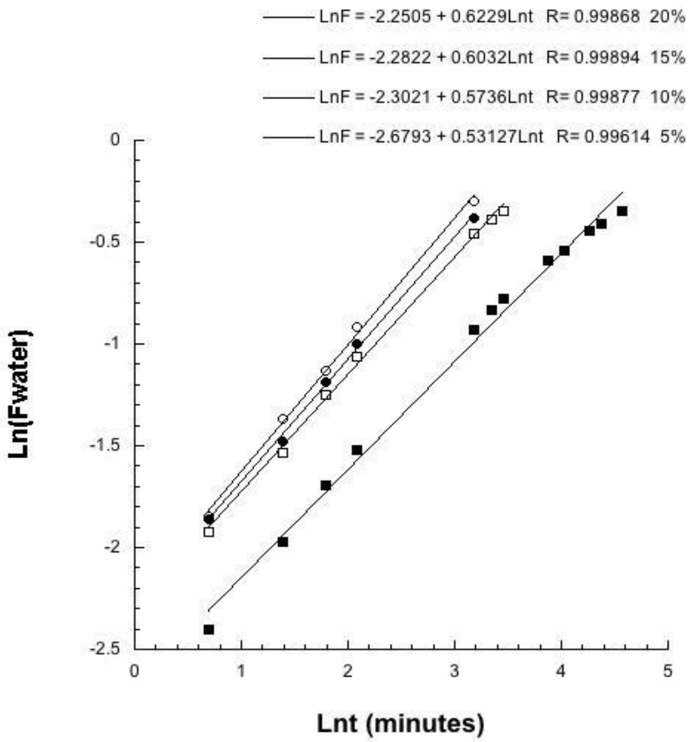

Figure C. Plot equation 12 for determining if the diffusion follows the law of Fick for hidrogeles place to solution of 100% saturation.