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Diffusion coefficients of sodium dodecyl sulfate in water swollen cross-linked polyacrylamide membranes

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Abstract

Diffusion of aqueous sodium dodecyl sulfate (SDS) across cross-linked polyacrylamide hydrogel membranes has been studied by electrical conductivity measurements. Initial rapid sorption of SDS (as unimer) into the membranes is observed. The effect of SDS concentration, and of cross-linker fraction on the degree of swelling of the gels is studied and associated with binding of the surfactant to the polymer, with surface bound water suggested to be involved in these interactions. Below the surfactant critical micelle concentration, volume collapse of less cross-linked membranes is observed, and associated with aggregate formation. Fluorescence measurements using pyrene as a probe show that micellar aggregates do not diffuse through the membrane, and only overall unimer diffusion is observed. The effect of cross-linking on the diffusion process is discussed.

Keywords: Hydrogels; Diffusion coefficients; SDS; Acrylamide

1. Introduction

The diffusion of solutes in hydrogels has applications in a wide variety of processes and systems, such as its use in biosensors [1], purification procedures [2], etc. Particular reference can be made to the application of hydrogels based on polyacrylamide and the anionic surfactant sodium dodecyl sulfate (SDS) in the electrophoretic separation of biological macromolecules (PAGE systems, see for example [3]). These varied applications result from the structural properties of the gels, and from the fact that they act as solid matrices with a very high water content, in which the different solutes can move without interactions with other species. For this reason, the gels also provide an ideal model system in which diffusion may be easily studied in the absence of convection, and from which it is postulated that the free solution diffusivities can be inferred [4].

In a previous study [5] we have found that water may play an important role in the behaviour of neutral gels based on acrylamide, due not only to non-neglected water-solute interactions, but also to the effect of water–polymer interactions on the water-solute behaviour.

In the present work, the influence of the monomer and cross-linker fractions on the transport of aqueous solutions of SDS was investigated in acrylamide-based non-ionic hydrogels with various degrees of cross-linking. A wide range (2×10^{-4} to 4×10^{-2} M) of surfactant concentration was studied, encompassing the critical micelle concentration (c.m.c. ≈ 8 mM) of the surfactant. The results show that the flux of the surfactant is clearly dependent on the water concentration inside the gel and that it increases with a decreasing of the water concentration. This unusual behaviour, which is similar to that obtained with polyelectrolyte gels, will be discussed in detail.

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2. Experimental

2.1. Preparation of the membranes

Acrylamide (AAm) and *N*,*N*′-methylene-bis-acrylamide (MBAAm), sodium persulfate, and SDS were obtained from Riedel-de-Haen, Fluka AG and Sigma, respectively.

The gel membrane was prepared by free radical copolymerisation of the monomers (AAm and MBAAm) in aqueous solutions, using the following procedure: a quantity of the cross-linker and the initiator sodium persulfate (in a percentage 0.1% (wt/v)) were added to a volume of acrylamide solution and stirred until total homogenisation was observed; the pre-gel solution was dropped inside two glass sheets, separated by a plastic rubber gasket; these were then joined using two spring clips. The mould is placed in an oven at 50 °C for 2 h. After this, the gel membrane obtained was removed from the gasket, placed between two plastic sheets, and stored inside a dessiccator at about 98% relative humidity.

The degree of swelling of the samples ($Q = w/w_0$) was estimated from the weights of dry PAAm (w_0) and of the swollen sample (w) and is equal to the volume ratio of the samples in the different stages. The value of w was measured in approximately 1 cm^2 samples, after being immersed for at least, two weeks in water or SDS solution. The solutions were prepared with water of conductivity $(1.2 \pm 0.4) \times 10^{-4}\ \Omega^{-1}\,m^{-1}$.

The relative volume ($\beta = V/V^*$) gives the volume alteration in the sample membrane, in equilibrium with water (V^*), due to SDS sorption.

Table 1 shows the composition of the synthesised membranes as well as the degree of swelling when in equilibrium with water, Q. For simplicity, the above membranes will be referred to by their symbols.

2.2. Sorption and desorption experiments

The concentration of SDS sorbed by the membrane, C, was calculated by measuring the concentration of surfactant in the aqueous solution prior to (c_0) and after (c_∞) the swelling experiments, using the expression

$$C = (c_\infty - c_0)V_{aq}/V \quad (1)$$

where V_{aq} and V are the volumes of the aqueous solution and membrane sample, respectively.

The membranes, which had previously been kept in equilibrium with water, were then immersed without stirring in the SDS solution for two weeks until they attained equilibrium. The approach to equilibrium was monitored gravimetrically (ADA analytical balance, with a resolution of 0.1 mg). Experiments were carried out in triplicate at 25 °C. Desorption experiments were carried out in a similar way: the polymeric membranes, after having reached equilibrium in electrolyte solution, were immersed in a known volume of water for approximately two weeks. The amount of SDS desorbed, as determined by conductivity, was then calculated.

Table 1
Chemical composition of the gels in the pre-gel solution, and the degree of swelling, Q, of the gels in equilibrium with water

Gel	[AAm] (M)	MBAAm/AAm (mol ratio, %)	$Q \pm s$
AA1	2.5	0.07	6.5 ± 0.6
AA2	2.5	0.007	24.8 ± 0.5
AA3	5	0.07	4.02 ± 0.07
AA4	5	0.007	6.34 ± 0.08
AA5	5	0.003	12.1 ± 0.1

2.3. Permeability technique

Permeability of SDS in polyacrylamide gels was measured using a cell similar to that previously reported [6] (Fig. 1). This consists of two compartments filled with SDS solution (A) and water (B), respectively. The hydrogel membrane (M), previously swollen in water up to equilibrium, was placed between the two cells. Silicone was used to seal the membrane to ensure hermetic interfaces. The SDS flux through the membrane was monitored by measuring the conductivity using a YSI 3200 apparatus, coupled to a conductivity cell with a cell constant of $K = 10\ m^{-1}$. The conductivity system was calibrated after each experiment. Identical conditions were used for calibration and permeability experiments. During each experiment, the solutions in the cells A and B were maintained at a constant temperature of 25 °C in a thermostatic bath (Velp Scientifica). The data were read at 2 min intervals over the time interval necessary to reach a SDS concentration in cell B (c_B) of approximately 2 orders of magnitude lower than that in cell A (i.e. $c_A/c_B > 100$). For maximum precision, the experi-

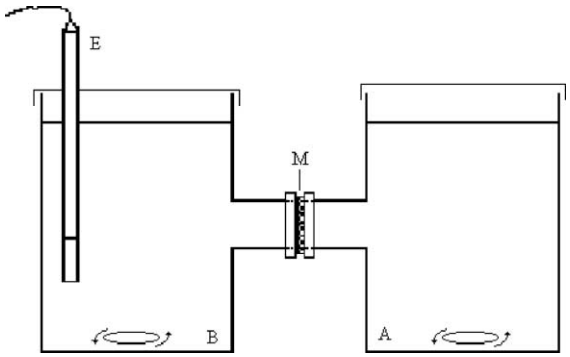

Fig. 1. Permeability cell. A and B are the compartments of surfactant solutions and water, respectively; M is the membrane; and E is the conductivity electrode.

mental conductivity data used to calculate the integral diffusion coefficients was taken from at least 300 points.

Allowance for retardation of diffusion near the polymer surface is essential in the case of hydrophilic polymers with a high water content, especially due to the formation of an immobile layer, the Nernst layer [7]. In Fig. 2, for example, we may note the effect of the membrane thickness on the SDS flux in two different systems: SDS(2×10^{-2} M)/AA2 and SDS(8×10^{-4} M)/AA3, when both solutions were stirred magnetically at 220 rpm. The experimental data were treated mathematically assuming that the SDS transport through gels is Fickian. Under these conditions, as a consequence of Fickś first law, we may write [8]

$$c_A/J = l_N/D_0 + l/P \quad (2)$$

where J is the amount of surfactant permeating the membrane per unit area during the time t, l_N is the Nernst layer thickness and D_0 is the diffusion coefficient of the surfactant in aqueous solution [9,10]. From Fig. 2 and Eq. (2), using the interdiffusion coefficients of SDS in aqueous solutions measured using the cell described by Lobo and co-workers [10], we can estimate values of $l_N = 1.52 \times 10^{-6}$ and 4.02×10^{-11} m for AA2 and AA3, respectively. In these experiments we have used gel samples of thickness approximately 1–2 mm. Here the effect of the Nernst layer can be neglected since it represents <0.1% of the membrane thickness and therefore is included in the experimental error of the diffusion coefficients (approx. 5%).

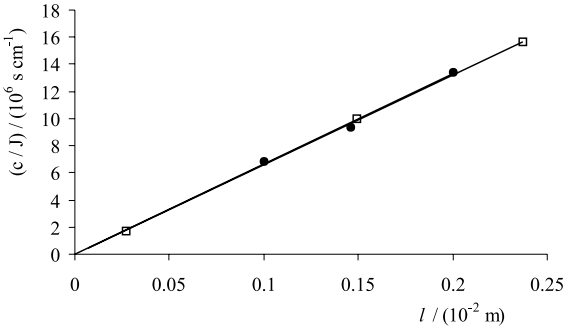

Fig. 2. Effect of the membrane thickness on the flux of SDS. (□) AA2, $l_N = 1.52 \times 10^{-6}$ m, $R^2 = 1.00$; (●) AA3, $l_N = 4.02 \times 10^{-11}$ m, $R^2 = 0.99$.

2.4. Fluorescence measurements

Fluorescence measurements, both on membranes and on diffusion across the membranes, were made using a Spex Fluorolog 111 spectrometer. Pyrene was dissolved in aqueous solutions of SDS, and its fluorescence monitored in solution in standard quartz 1 cm^2 cuvettes using excitation at 337 nm. For studies of SDS permeation across the membrane, aliquots of solution after the membrane were taken, and the fluorescence spectra measured at various times. Over the time range studied (up to two days) there was no evidence of any pyrene diffusion across the membrane.

3. Results and discussion

3.1. Effect of SDS on the gel properties

The effect of SDS concentration on the volume and mass of the membranes was studied. Table 2 and Fig. 3 show the variation of the degree of swelling and relative volume as a function of SDS concentration, respectively.

The effect of SDS concentration on the degree of swelling, Q, and on the relative volume, β, is approximately the same. The effect of these two dependent parameters seems to be related to the water concentration inside the gels as well as to the ratio of monomer to cross-linker. The effect of the cross-linker on the degree of swelling and volume collapse is greater with the gels prepared with AAm 2.5 M (AA1 and AA2) than with those using AAm 5 M (AA3–AA5). This can be justified by the topological interactions occurring between polar acrylamide groups on the two chains which lead to a more rigid structure which effectively works as further cross-linking. Consequently, the effect of the

Table 2
Degree of swelling (Q) of different polyacrylamide membranes in SDS solutions

c(SDS) (M)	$Q(\pm s)$				
	AA1	AA2	AA3	AA4	AA5
8×10^{-4}	6.13 ± 0.04	21.6 ± 0.2	4.01 ± 0.05	6.48 ± 0.13	12.5 ± 0.5
1×10^{-3}	6.17 ± 0.09	20.9 ± 0.4	3.99 ± 0.03	6.45 ± 0.07	12.6 ± 0.4
2×10^{-3}	6.20 ± 0.07	20.2 ± 0.6	3.99 ± 0.12	6.43 ± 0.10	12.5 ± 0.3
5×10^{-3}	6.13 ± 0.02	19.5 ± 0.0	3.97 ± 0.02	6.29 ± 0.04	12.5 ± 0.1
8×10^{-3}	6.10 ± 0.08	18.1 ± 0.4	3.96 ± 0.04	6.19 ± 0.12	12.2 ± 0.1
1×10^{-2}	6.09 ± 0.02	17.1 ± 0.5	3.97 ± 0.01	6.07 ± 0.02	12.0 ± 0.2
2×10^{-2}	6.11 ± 0.02	16.7 ± 0.3	3.97 ± 0.02	5.95 ± 0.13	11.8 ± 0.1
4×10^{-2}	6.06 ± 0.06	15.5 ± 0.2	3.96 ± 0.08	5.86 ± 0.06	11.4 ± 0.2

cross-linking is greater with the less concentrated monomer gel. The volume collapse is most marked in the gels AA2 and AA5, which are weakly cross-linked and, therefore, characterised by having a high content of water. The effect of SDS on the gels AA2 and AA5 is also very important, and these gels still show the effect at the highest swelling pressure—high swelling degree. From the experimental data of Q and β we can see that the variation of such parameters is most marked at SDS concentrations above the critical micelle concentration (cmc).

From Figs. 3 and 4, we may also conclude that there is a rapid incorporation of surfactant in the membrane. The relative volume ratio, β, in equilibrium with SDS solution is reached within the first hour of immersion. This rapid sorption can be justified either by a surface process or by a fast diffusion process [11] followed by a reorganisation of SDS aggregates inside the polymer matrix which provokes the collapse of the membrane structure. From Fig. 4 we can observe that the SDS–gel equilibrium is reached more slowly in gels that are less cross-linked and which show a higher percentage of water uptake. This suggests that the mobility of the network structure [12,13] in such gels can play an important role in the re-organisation and in the re-orientation both of the SDS species, and of the polymeric structure itself.

From fluorescence spectra of pyrene solubilized in an aqueous solution of SDS at a concentration (4×10^{-2} M) above the cmc, and for the same solution in equilibrium with polyacrylamide (AA2) the intensity ratio (I_3/I_1)—a direct measure of polarity changes in the polymeric membrane [14]—for Py in SDS is 1.02, while for the system containing PAAm it is 1.04. Assuming the uncertainty of such ratio as ± 0.02 [15], we may conclude that there is no alteration in the polarity of the medium that the Py sees, and consequently there are no interactions between the micelles and PAAm. Similar results

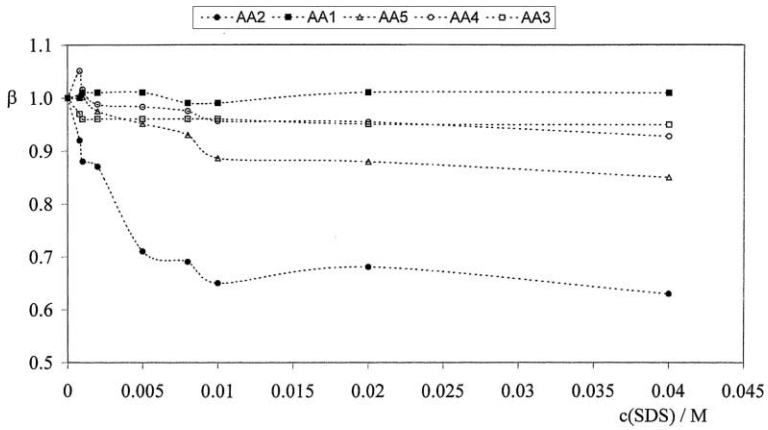

Fig. 3. Effect of the SDS concentration on the relative volume, β, of the polyacrylamides.

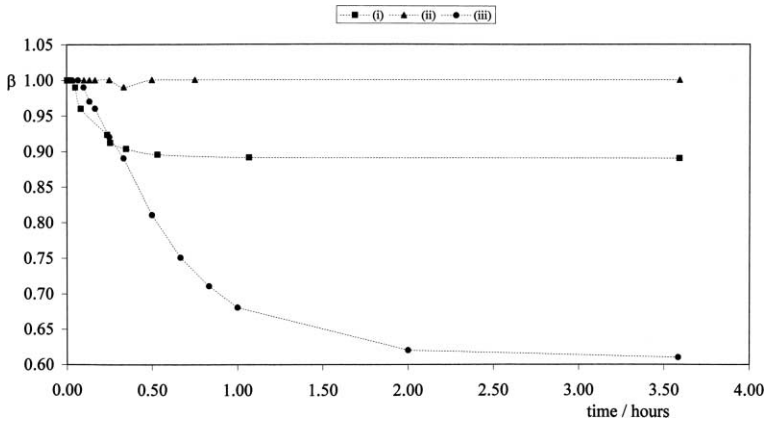

Fig. 4. Examples of the effect of SDS sorption on the relative volume ratio, β, of the hydrogels. (i) SDS(4×10^{-2} M)/AA4; (ii) SDS(4×10^{-2} M)/AA1; (iii) SDS(4×10^{-2} M)/AA2.

were observed with the other polyacrylamide membranes. This is in good agreement with the Nernst layer analysis previously presented.

3.2. Sorption isotherms

To obtain more details of the thermodynamic features of SDS/gel systems, sorption experiments were carried out. The sorption isotherms of the polyacrylamide hydrogels prepared with 2.5 and 5 M acrylamide are shown in Figs. 5 and 6, respectively. The experimental error of the average values (shown in Figs. 5 and 6) is <7%.

From Figs. 5 and 6 we can see that whilst in the PAAm from 2.5 M AAm there is no effect of the cross-linker on the SDS sorption isotherms, in the membranes with a higher content of AAm the effect of MBAAm content is clear. The dependence of C on SDS concentration needs a more detailed analysis. Taking the cmc of SDS as a concentration reference (8.3×10^{-3} M [16]), we may note that at concentrations below the cmc, the gel with a higher water content can dissolve more SDS, whilst the concentration values for SDS in the other two gels are approximately the same, in agreement with the values for the degree of swelling. In contrast, at concentrations above the cmc, the values of C do not show any clear dependence on water content.

From the experimental data of sorption, we may observe that at SDS concentrations below the cmc there is an accumulation of SDS inside the gel (when $c <$ cmc then $C > c$) which is not followed at concentrations higher than the cmc. The interaction between the surfactant and the polymer groups (physical or chemical

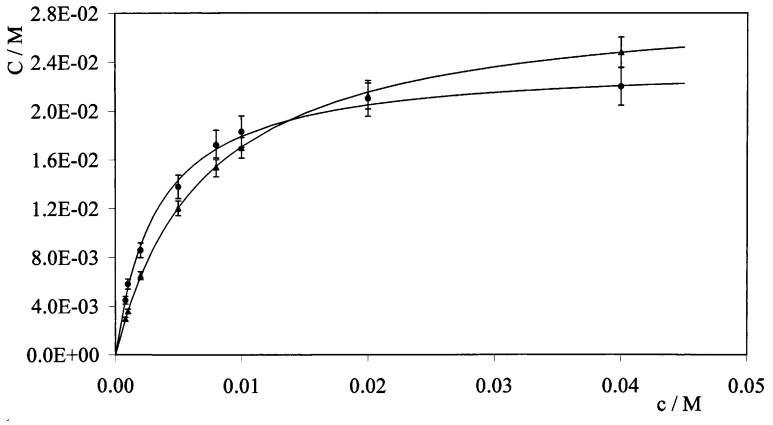

Fig. 5. Sorption isotherms of SDS in polyacrylamide membranes with acrylamide 2.5 M: (●) AA1; (▲) AA2. The fitting lines were obtained by linear regression of the Langmuir equation to experimental data (see Table 3).

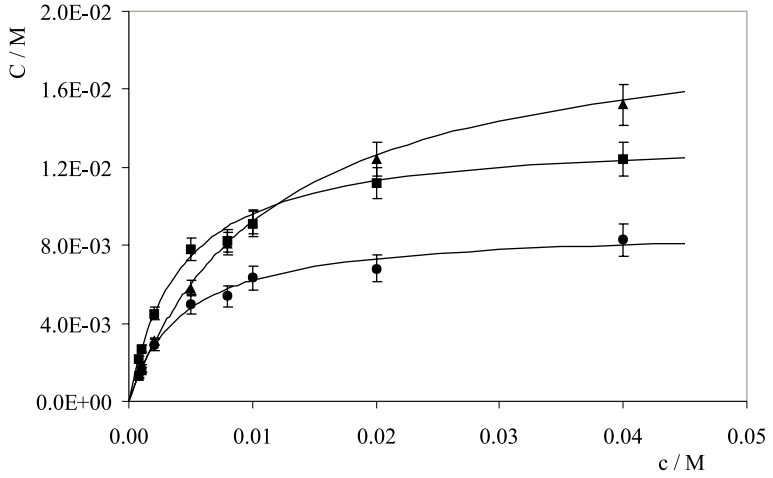

Fig. 6. Sorption isotherms of SDS in polyacrylamides with acrylamide 5 M: (■) AA3; (●) AA4; (▲) AA5. The fitting lines were obtained by linear regression of the Langmuir equation to experimental data (see Table 3).

Table 3
Linear regression for fitting the experimental data (Figs. 5 and 6) to Eq. (3), with a 90% confidence interval

	$m \pm ts_m$	$(b \pm ts_b)$ (M^{-1})	R^2	K'	C' (M)
AA1	0.14 ± 0.00	41.6 ± 2.6	0.994	7.1	3.3×10^{-3}
AA2	0.24 ± 0.00	34.2 ± 0.5	1.000	4.1	7.1×10^{-3}
AA3	0.31 ± 0.01	74.5 ± 3.7	0.999	3.3	4.1×10^{-3}
AA4	0.48 ± 0.01	112.6 ± 4.3	0.999	2.1	4.3×10^{-3}
AA5	0.58 ± 0.01	50.1 ± 3.8	0.998	1.7	1.2×10^{-2}

s_m and s_b are standard deviation of slope and intercept of linear regression of $1/C$ as function of $1/c$, respectively; t: quantity used in the calculation of confidence limits using a t-distribution; R^2: correlation coefficient; m: gradient of regression line ($m = 1/(C'K')$); b: intercept of regression line ($b = 1/C'$).

sorption, immobilisation, formation of complexes involving water, etc.) can be generally described in terms of Langmuir sorption. Thus in general, sorption of SDS can be described by equation

$$C = C'K'c/(1 + K'c) \tag{3}$$

where C' represents the concentration of solute molecules that could be sorbed in specific sites of a polymer at saturation conditions, and K' is the corresponding equilibrium constant. The isotherms of SDS sorption by different gels shown in Figs. 5 and 6 confirm the Langmuir character of sorption. The fitting parameters of the experimental data using Eq. (3) are presented in Table 3.

From analysis of the data in Table 3 we can conclude that C' increases with a decrease of cross-linker concentration for each set of PAAm (2.5 and 5 M) and that the equilibrium constant increases with an increase of both cross-linker concentration and AAm concentration. These results, therefore, show that the interaction between the SDS and the polar groups of AAm is stronger in the less concentrated gels. We may expect that the polar part of the surfactant molecules interact more strongly with the polar groups of acrylamide when the free volume available for dissolving SDS decreases. This is supported by the fact that although the membranes AA3–AA5 have initially more polar groups derived from AAm, the majority of these are not available to interact with the polar part of SDS due to the formation of so-called topological cross-linking.

Associating the sorption isotherms with the volume changes during the sorption process, we may justify the behaviour of SDS in the sorption isotherms. It is well known that the less cross-linked hydrogels show a mobility of their chains [17] and that this mobility decreases with increasing cross-linker content. As an example we can consider the gel AA5: this gel shows a very high C' and a higher volume decrease when in equilibrium with SDS solution. We expect that if there is another gel showing higher SDS C values at concentrations, c, above the cmc, then the collapse of the membrane must have influence on the sorption equilibrium concentrations.

According to the above discussion we suggest the following mechanism of sorption: (a) the SDS unimers can enter in the matrix and interact first with some polar sites of the polymer matrix; (b) at concentrations of SDS below the cmc, the unimers are trapped by the matrix and the volume collapse of the less cross-linked membrane occurs which suggests the formation of aggregates and the consequent relaxation of the membrane structure; (c) at concentrations around and above the cmc some unimers can enter the aqueous medium of the matrix, while maintaining equilibrium with the unimers in solution and the volume changes stop. We will show that this is in agreement with the fact that micelles do not cross the hydrogel membranes. Pyrene shows a very low solubility in water, but does dissolve appreciably in SDS micelles. If micelles cross the hydrogel membrane, they will also transport pyrene. That this does not occur is seen very clearly using fluorescence to monitor pyrene as a probe for micelle transport across the membranes. We have studied the permeation of SDS (4×10^{-2} M) in the presence of dissolved pyrene with the polyacrylamide AA2 and AA3 for approximately three days. The measured fluorescence of the post-membrane solution after this time clearly shows that no pyrene has crossed the membrane, indicating that only the unimeric SDS molecules are able to go through the polymeric matrix. Within the matrix, however, the structure favours the formations of stable aggregates from these unimers.

There are two possibilities to interpret the experimental results and the proposed model: (a) the sorption of the SDS by the gel is followed by a rearrangement of the SDS structure; (b) the surfactant can react with polymeric network forming a supramolecular structure similar to that reported to charged gels and surfactant systems [18].

Hypothesis (b) is characterised by a rapid decrease in the volume ratio of the polymeric matrix [18] as well as by the formation of strong bonds between the polymeric chain and the surfactant. However, desorption experiments have shown that the concentration of the desorbed surfactant in all systems is equal to the concentration of the sorbed surfactant. In these circumstances, the process of sorption at specific polar sites

of the polymer is reversible and the formation of a supramolecular structure does not occur, and hypothesis (a) will be considered as more likely. With this model, another question arises: What kind of bond exists between SDS unimers and the polar sites of the polyacrylamide structure, which are then responsible for the Langmuir-type sorption? In a previous study [19] we have found that water has an important influence in the whole process of transport of non-associated electrolytes in these gels. Water shows a variety of different structures in these gels [20]. The dissolution of a solute in such a medium affects these structures, and consequently the free energy of the system [21]. Therefore, the interaction of the polar group of the SDS unimer with the polar sites of acrylamide does not occur directly but via water molecules, specifically the so-called non-freezing water molecules. This will explain the complete reversibility of the sorption process.

3.3. Kinetic studies

The flux of SDS through polyacrylamide membranes is shown in Fig. 7. This was obtained using the permeability technique under steady-state conditions. The flux, F, was calculated using the equation:

$$F = Jl = (V/A)\mathrm{d}c/\mathrm{d}t \quad (4)$$

where $\mathrm{d}c/\mathrm{d}t$ is the variation of SDS concentration crossing the membrane as a function of time, A is the cross-sectional area of the membrane, and V is the volume of SDS solution.

The flux process in the gels can be explained by the entrance of unimers in the matrix, possibly forming small aggregates that are responsible for the mass transport. At concentrations above the cmc, the micelles cannot enter inside gel and the concentration of surfactant in gel is not sharply affected. For this reason, a smaller increase in the flux occurs.

From Fig. 7 we may also observe that the effect of the cross-linking on the flux of SDS is dependent on acrylamide concentration. In fact, in the polyacrylamide synthesised with AAm 5 M (AA3–AA5), the transport of SDS is dependent on the degree of swelling, which is effectively proportional to the available free volume. We should note, however, that the presence of the network structure as well as the possible interactions with different water molecules and structures [20] may also be responsible for the retardation of the permeability process. We can also see that the highest increase in the swelling degree (from AA4 to AA5) is followed by the highest increase of the flux. The flux of SDS through AA1 and AA2 shows two distinct regions: at SDS concentrations below 8×10^{-3} M the fluxes are equal, which suggests that there is a balance between the type of diffusing species and the free volume. At concentrations above the cmc, the flux of SDS through AA1 is enhanced comparing with AA2. This phenomenon can be explained by the increase in the network density due to the collapse of the gel (much more significant in the gel AA2) and, as a consequence, an increase of steric interference to surfactant permeation may occur. This may explain the reversibility of the surfactant sorption uptake [22] as well as supporting the idea that the formation of links between the surfactant and the polymer structure occurs via water.

The experimental results described in this and previous sections suggest that the diffusion of SDS depends not only on C but also on the immobilised SDS species

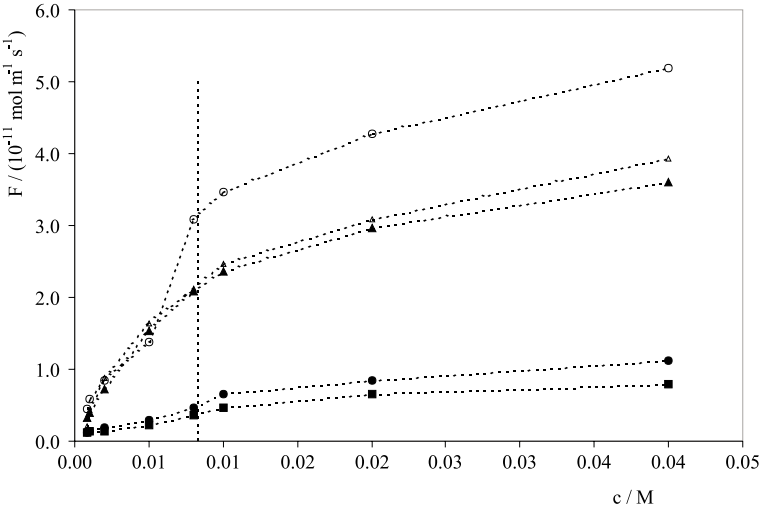

Fig. 7. Dependence of the flux, F, on the surfactant concentration, at 25 °C. (○) AA1; (△) AA2; (■) AA3; (●) AA4; (▲) AA5. The dashed line shows the cmc of SDS in aqueous solution.

inside the polymer. Although some cases have been described in literature of effective immobilisation of different ions in hydrogels [23], in the present systems the immobilization of surfactant seems a rather complex concept. At the same time the gel swelling and shrinking processes are not pure diffusion processes. In fact the total energy of a gel depends on bulk and shear energies. Whilst the later can be minimised by readjusting the shape of the gel, the bulk energy is controlled by diffusion. Different models, as for example the Li-Tanaka model [24] and the differential swelling stress model [25], have been used in order to take into account such simultaneous phenomena. Once experiments were carried out on steady-sate conditions, where the swelling degree changes are not significant, we may postulate the following assumptions in order to calculate the integral diffusion coefficient, D_{eff}: (a) a local equilibrium between the adsorbed unimers (in aggregate or unimer form) and unimers (in aqueous solutions) occurs; (b) the formation and destruction of micelles or aggregates are much faster than surfactant diffusion [26]; (c) under the steady-state conditions, the volume change of the gel is ignored [27].

Following these assumptions the steady-state integral diffusion coefficients of SDS can be calculated on the basis of the Fick's first law approximation, taking into account the steady state rates J and the SDS concentration in equilibrium with the gel C, according to

$$J = D_{\text{eff}} C/l \tag{5}$$

and using the overall concentration drop across the membrane, C, as determined by the sorption experiments, in terms of contiguous solutions; the concentration of the solution in cell B (the receiving compartment) is taken as zero.

As a first approach, the experimental data of D_{eff} shown in Figs. 8 and 9 reveal that the integral diffusion coefficients of SDS in PAAm are dependent on both cross-linker and monomer concentration. The integral diffusion coefficients also are of the same order of magnitude of the mutual differential diffusion coefficients, D_0, of SDS in aqueous solutions [10].

In an attempt to show how the diffusion coefficients depend on the cross-linker concentration, the polymer volume fraction, φ, was calculated using [28]

$$\varphi = \{1 + [(Q-1)\rho_p/d]\}^1 \tag{6}$$

assuming that all sorbed SDS has a density, d, similar to that in aqueous solutions [29]. The polymer densities, ρ_p, of gels AA1–AA5 are 249 ± 10, 422 ± 18, 202 ± 8, 241 ± 7 and 364 ± 28 kg m^{-3}, respectively. The polymer density values were calculated assuming water density in the gels equal to 1000 kg m^{-3}.

From Eq. (5) we may conclude that in the most concentrated gels (AAm, 5 M) the polymer volume fractions change from 0.63 (AA3), 0.43–0.46 in the AA4, to 0.19–0.21 in AA5. This shows that a possible inter-

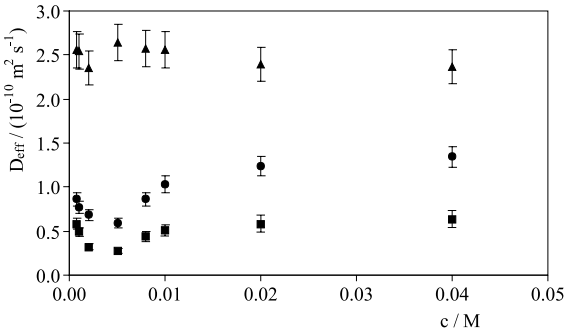

Fig. 9. Steady state integral diffusion coefficients of SDS, D_{eff}, in the polyacrylamides with AAm 5 M: (■) AA3; (●) AA4; (▲) AA5.

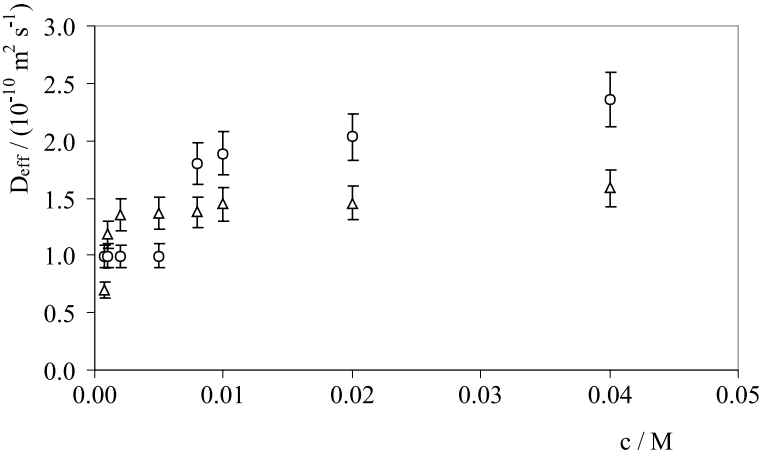

Fig. 8. Steady state integral diffusion coefficients of SDS, D_{eff}, in the polyacrylamides with AAm 2.5 M: (○) AA1; (△) AA2.

pretation of the D_{eff} (Fig. 8) may be made on the basis of the free volume concept.

In the gels with $\varphi = 0.63$ and approx. 0.43 the D_{eff} increase with an increase of free volume. However at concentrations around the cmc the variation of the diffusion coefficients suggests that some aggregates are responsible for a small variation of D.

When the polymer volume fraction increases to its highest value, approx. 0.20, there is no alteration of D_{eff} with the concentration. This may be due not only to aggregate formation but also to an alteration of the membrane structure as a function of concentration. A further possible reason for such behaviour is that aggregates or micelles have high surface charge densities, they attract counterions and, consequently, the diffusivity of such species in a highly cross-linked gel is much smaller than that of unimeric surfactant [30].

However, such a tendency does not occur in the gels AA1 and AA2, that is the dependence of diffusion coefficients on concentration does not simply depend on the free volume as was calculated in Eq. (6). The diffusion coefficients of SDS in the gel AA2 are approximately constant at $c <$ cmc, showing that the diffusing species have the same features. Although no alterations in φ occur at concentrations above the cmc, there is an increase in D_{eff} to values very similar to those obtained in aqueous solutions, showing that the aggregates are predominant in the diffusion transport. This explanation cannot be used for the mechanism transport of SDS in the gel AA2. Here, the effect of aggregate formation can be observed earlier, with a clear increase of D_{eff} as a function of concentration. However, such an increase is limited by the cmc, and at concentrations above the cmc, D_{eff} not only tends to be constant but is also lower than those obtained in AA1. The explanation can be found both by the formation of aggregates and also in the characteristics of a less cross-linked gel. At $c >$ cmc, due to the lower rigidity of the gel structure the possible SDS/gel interactions may reduce the real free volume relative to the diffusion process and, as a consequence, the SDS molecules are stabilised by polar groups of gel or by the water molecules [31], which act as an obstacle by steric hindrance retarding the diffusion process.

4. Conclusions

The present results suggest that SDS can change the swelling properties of the neutral gels. The SDS–water–gel interactions are dependent on the hydrophilic character of the network structure as well as of the surfactant properties. This SDS behaviour is well established in charged gels [32–34]. In fact, the charged swollen polymer gels form stable complexes with oppositely charged surfactants [34,35]. The formation of such complexes results in aggregation of the surfactant ions at concentrations below the cmc in solution [36]. Such interactions generally result, for example, in the collapse of the gel structure [27] and changes in the structure of surfactant aggregates [33]. These phenomena were found in this work, where the interactions depend both on the degree of cross-linking and the initial monomer concentration. Water is shown to be crucial for these effects. Of particular importance are the surface bound, or so-called non-freezing water molecules, which facilitate binding of surfactant molecules to the polymer membrane. This has marked effects on the diffusion of surfactant across membranes of such polymers.

Although a qualitative analysis has been made in order to explain the variation of the integral diffusion coefficients further work is needed to find a feasible quantitative explanation. Such an approach will lead to a better understanding of the diffusion mechanism involving further processes, including, for example, the mobility of the gels structure and the type of bonding between surfactant unimers and/or aggregates and the hydrogel structure.

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