Combined sorption/transport of sodium dodecyl sulfate and hydrochloric acid in a blend of cellulose acetate butyrate with cellulose acetate hydrogen phthalate

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Abstract

The transport of hydrochloric acid (0.001–0.1 M) and sodium dodecyl sulfate (0.001–0.1 M) has been measured through a membrane consisting of a blend of cellulose acetate butyrate and cellulose acetate hydrogen phthalate. The cellulose derivative blend is suggested to suffer an alteration in the degree of hydrophobicity when in equilibrium with sodium dodecyl sulfate (SDS) through hemimicelle formation. An increase in surface hydrophobicity of the blend when in equilibrium with SDS solution was observed by fluorescence measurements using the vibronic bands of the probe pyrene, as well as by water desorption kinetics; a decrease of the effective diffusion coefficients from 1.2×10^{-11} m^2 s^{-1} in the absence of SDS to approximately 2×10^{-13} m^2 s^{-1} in its presence was found. The value obtained for the mutual diffusion coefficient of HCl in the concentration range 0.001–0.1 M ($D = 4.2 \times 10^{-14}$ m^2 s^{-1}) shows also that the membrane presents hydrophobic features. The flux of SDS in the blend membrane at different pH values shows two distinct permeation rates depending on the cmc. However, from the calculation of permeability coefficients at SDS concentrations below the cmc a clear decrease in P is found, whilst, at concentrations above the cmc the permeability coefficients are nearly constant, only showing a slightly increase. The diffusion coefficients of SDS in the blend increase over the whole SDS concentration range analysed and show an effective diffusion coefficient 2–3 orders of magnitude below the diffusion coefficients of SDS in aqueous solutions. This fact suggests that the only diffusing species are SDS unimers. The presence of HCl in the SDS bulk solution has the effect of increasing the permeability and diffusion coefficients. Mutual analysis of permeation and diffusion coefficients and sorption isotherms shows that, on decreasing the pH, the interactions between SDS and the polymer network decrease. This is also reflected in a clear decrease of the hydrophobic interactions between the diffusing and polymeric species, provoked by a decrease in the unimer–unimer association.
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1. Introduction

Polymer membranes find applications in areas as varied as separation science [1], sensors [2] and surface coatings [3]. Particular interest is devoted to surfactant–polymer systems relevant to various areas, including formation of gels for use as thickeners [4–8], and in

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textile [9] and paper [10] processing. Diffusion of electrolytes across such membranes is important in many of those areas, such as in optimising conditions for separation processes and understanding the basic mechanisms involved.

We have previously reported [11] that cellulose ester blends, based on cellulose acetate butyrate (CAB) and cellulose acetate hydrogen phthalate (CAHP), show an interesting selectivity to SDS permeation, which depends on the hydrophilic/hydrophobic balance in the blend composition and on the temperature. In order to study the effect of SDS micellization as well as to extend the analysed SDS concentration range to more dilute concentrations, we have chosen the more hydrophilic blend; the effect of acidification of the bulk solution is also studied to check its effect in SDS structure and in the polymeric blend. Our final scope is to find appropriate membranes for separation by either changing the hydrophobic/hydrophilic balance in the blend, or altering in a simple way (e.g., changing pH) the solution.

The transport of SDS is analysed by a method originally developed for calculating diffusion coefficients of electrolytes [12–14] from electrochemical conductivity measurements. This method is applied to the study of diffusion of electrolytes in polymer membranes [13,14]. We are particularly interested in the behaviour of ionic surfactants, and we have previously studied the diffusion of the important anionic detergent sodium dodecyl sulfate (SDS) in poly(acrylamide) gels [15] and in cellulose ester membranes of differing degrees of hydrophobicity [11].

We will show how pH alterations might affect the SDS permeation. Experiments were carried out using solutions of SDS (10^{-3}–10^{-1} M) mixed with HCl (10^{-3}–10^{-1} M) to evaluate how the pH affects the SDS permeation. In addition to their application to the present system, these studies are also important in more general terms since the transport of mixed solutes has received little attention and is a very important feature for the characterisation of mass transport processes occurring in polymeric matrices.

2. Experimental

2.1. Reagents

The chemicals used were from the following sources: cellulose acetate butyrate (CAB) containing 17% butyrate, cellulose acetate hydrogen phthalate (CAHP) and tetrahydrofuran +99.9% (THF) from Aldrich; sodium dodecyl sulfate (SDS) from Merck; and potassium chloride and hydrochloric acid 32% from Riedel de-Häen. All low-molecular weight compounds are of ProAnalysis quality and were used without further purification. The solid KCl was weighed after drying the salt until constant weight at 110 °C.

Concentrated SDS solution was obtained by dissolving the corresponding amount of solid in bi-distilled water of conductivity 1.2 $(0.4) \times 10^{-4}$ Ω^{-1} m^{-1}, and standard solutions of different concentrations were prepared from this by dilution.

2.2. Membrane preparation

The CAB/CAHP blend films were obtained by initially dissolving CAB (33.3% w/v) and CAHP (66.7% w/v) in THF, at a concentration of 10% (weight of polymer/volume of solvent) and stirring for 24 h to ensure homogeneity. The homogeneous solution was then deposited as a film on a flat glass support using a Simex automatic film applicator. Specific moulds were used to prepare membranes with a homogeneous thickness. After complete evaporation of the solvent at room temperature, the membrane was removed from the glass support with the help of water. Characterisation of the blend shows a certain degree of mixing of the two polymers, since the density of the blend (0.850 g cm^{-3}) is lower than that of either CAHP (0.902 g cm^{-3}) or CAB (0.940 g cm^{-3}), and the differential scanning calorimetry (DSC) curve of the blend film is also different from that of the two pure polymers (Fig. 1).

2.3. Differential scanning calorimetric analysis

The samples (2 mg weight) were cut from films which were prepared as described above. To remove the residual solvent, the films of pure polymers and blend were dried at reduced pressure for, at least, one day at ambient temperature. Differential scanning calorimetry measurements were performed using a *Shimadzu* differential scanning calorimeter, *DSC-50* model, at a heating
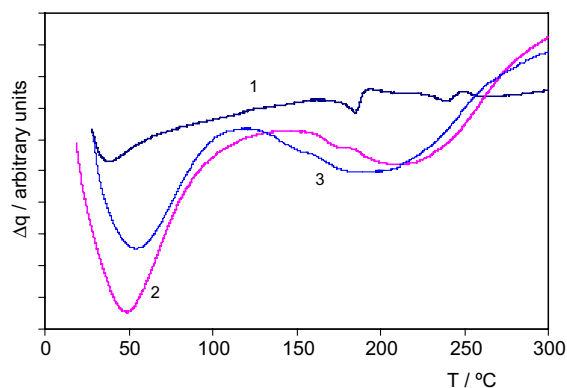

Fig. 1. DSC curves obtained for films of cellulose acetate butyrate (1), cellulose acetate hydrogen phthalate (2) and CAB/CAHP blend (3).

rate of 20 °C/min, in a nitrogen atmosphere flowing at 20 mL/min. The thermograms (Fig. 1) were obtained after the following treatment: heating from ambient temperature to 300 °C and posterior cooling to ambient temperature and maintained on this temperature for 5 min.

2.4. Permeation experiments

The transport of SDS, HCl and their mixture through the membranes was measured by using a permeation cell as described previously [16,17]. This consists of two cells filled with a permeant solution (cell A) and water (cell B). These are connected by two horizontal tubes, and the polymer membrane is placed between them. Silicone was used to seal the membrane to ensure hermetic interfaces. The experiments were carried out ensuring that there is streamlined flow near the membrane, and that there is no hydrostatic pressure influencing the transport.

The variation of concentrations of binary systems of SDS and HCl was determined in cell B during permeability experiments by measuring the electrical conductivity using a YSI 3200 instrument. During the multicomponent transport of SDS/HCl mixtures, the flux of the diffusing species was monitored both by measuring the electrical conductivity and by a potentiometric technique using a liquid membrane chloride selective (*Orion, Ref. 93–17* with a detection limit of 5×10^{-6} M) and combined pH electrodes, with a Radiometer PHM240 pH meter (pH resolution 0.001, electrode potential resolution 0.1 mV). All the pH values were corrected by measuring the electrode sensitivity as well as the zero pH. The variation of electrical conductivity in cell B was monitored continuously. However, it was not possible to use this approach for pH and chloride electrode potential measurements because of possible artefacts caused by doping of the electrodes at the electrolyte concentrations studied over the long time scales used in these studies. Instead, the following procedure was used: after the beginning of each experiment, 10 mL aliquots of solution were taken from cell B at fixed intervals of time. These were diluted with bi-distilled water and the chloride and hydrogen ion concentrations were measured potentiometrically. The total ion concentration in cell B was calculated from the electrical conductivity data, while the concentrations of H^+ and Cl^- were obtained from the potentiometric measurements. Within experimental error, the proton and chloride concentrations were identical, showing that HCl can be considered to diffuse as a single entity. Thus, according the electroneutrality principle [18], the SDS concentration can be calculated subtracting the concentration of HCl from the total concentration of diffusing species.

The flux of each component of the solution, J_i, with i representing HCl or SDS, was calculated according to

$$J_i = (V/A)(\mathrm{d}c_i/\mathrm{d}t) \tag{1}$$

where V and A are the volume of the solution in cell B (200 mL) and the permeating area (1.54 cm^2), and $(\mathrm{d}c_i/\mathrm{d}t)$ is the variation of the concentration of the i-species, in cell B, with time t. The thickness of each membrane ($l \cong 20$ μm) was measured after each experiment and showed no variation resulting from swelling.

The conductivity and potentiometry instruments were calibrated (i.e., the dependence of the electrical conductivity, pH and electrode potential on the SDS, HCl and KCl concentrations, respectively) prior to each experiment using, at least, four standard solutions, whose concentration range covered the range of experimental values being measured in cell B. The concentrations of HCl solutions were accurately determined by volumetric titration with a standard solution of sodium tetraborate.

The same experimental conditions were used for calibration and permeability experiments: solutions were stirred at ≈220 rpm, and constant temperature (25 ± 0.1 °C) was maintained by using a VelpScientifica Multistirrer 6 thermostat bath. Data were recorded over a sufficient time to ensure a steady-state flux, but such that the diffusant concentration in cell B was always well below the cell A concentration (<10%).

2.5. Water desorption

All gravimetric measurements on water desorption were made to ±0.1 mg using a Sartorius Analytical balance. Different samples of the same membrane were placed in water for approximately 2 weeks. Following this, the membranes were rinsed with distilled water, excess moisture was wiped off, and samples placed inside a 10^{-2} M SDS solution for 120 h. After this equilibrium time (gravimetrically controlled) the membranes were removed and excess moisture was wiped off. The loss of weight with time under vacuum at 25 °C was monitored gravimetrically. The weight/weight (w/w) water concentration in the membrane, C_{wt}, at time, t, was calculated from

$$C_{wt} = M_t - M_\infty / M_t \tag{2}$$

where M_t is the weight of the sample at time t and M_∞ is the weight of the dried sample, obtained after the complete desorption of water to a constant value. The initial weight/weight (w/w) water concentration (C_{w0}) is obtained at $t = 0$.

The effective water diffusion coefficients, D_{weff}, were computed using a Fickian approach to fitting the water desorption curve (Fig. 2)

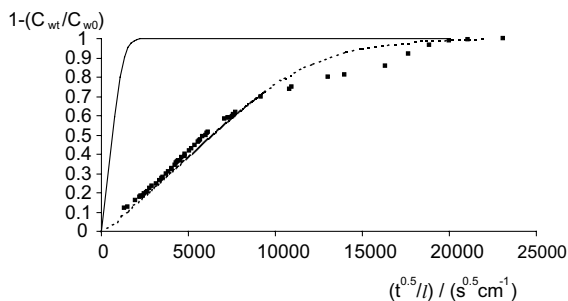$$1 - (C_{wt}/C_{w0}) = 4(D_{weff}t/\pi l^2)^{0.5} \tag{3}$$

Fig. 2. Desorption kinetics of water from CAB/CAHP blend membranes in water (—), [11] and in 10^{-2} M SDS solution (●). The dashed lines were obtained from fitting Eq. (3) to the experimental data.

where l ($= 0.040$ mm) is the thickness of the membrane, measured using a Helias micrometer (0.005 mm).

2.6. Sorption experiments

Different samples (square geometry of well-defined area, $A' = 25$ cm^2) of the same membranes were cut, immersed in water at 25 °C until equilibrium was reached (2 weeks). Following this, they were transferred to SDS, HCl or mixture solutions, with volumes of 40 mL, and left to reach equilibrium (3 weeks). Subsequently, the membranes were removed and their thickness, l, was measured. When no more swelling was observed, the polymer volume, V_P, was then calculated from A' and l. The approach to equilibrium was controlled gravimetrically.

The concentration of the SDS, HCl or SDS + HCl sorbed by the membrane, C, was calculated using

$$C = (c_\infty - c_0)V'/V_P \qquad (4)$$

by measuring the concentration of the sorbed species in aqueous solution of a volume V' prior (c_0) and after (c_∞) the sorption experiments, using the same techniques described in the previous section.

The average values of C were obtained from three independent measurements.

2.7. Fluorescence measurements

Fluorescence measurements on membranes were made using a Spex Fluorolog 111 spectrometer, with samples mounted in 1 cm^2 quartz cuvettes and excitation at 337 nm. A sample of the polymeric blend was immersed in an aqueous solution of pyrene (Py, 10^{-5} M) in SDS (10 mM) overnight, removed and then its fluorescence spectrum measured. Fluorescence was also used to study diffusion of SDS across the membranes by measuring the spectra of aliquots of solution from cell B in 1 cm^2 quartz cuvettes.

3. Results and discussion

3.1. Effect of SDS on polymer blend hydrophobicity

Fluorescence studies were carried out on the membranes using pyrene (Py) as a probe, and studying the spectrum after immersion of the membrane in SDS solution. Relative intensities, I_1/I_3, of the first and third vibronic bands of pyrene fluorescence, which are a measure of local polarity [19,20], were measured for the systems Py/polymer membrane/SDS as a function of immersion times of the membrane samples in SDS (0.01 M) solution. When the immersion times of the membrane in SDS solution were 1, 7 and 11 days the corresponding relative intensities I_1/I_3 were 1.59 (±0.02), 1.43 (±0.01) and 1.32 (±0.02), respectively. These results show that there is an increase of the surface hydrophobicity of the polymer [19] with time of immersion of the membrane. The effect of the surfactant on the membrane hydrophobicity can be accounted for using the concept of hemimicelle (HM) formation [21]. Hemimicelles have previously been observed on adsorption of SDS on solid surfaces, such as alumina, by fluorescence probes [22], electron spin resonance spectrocopy using nitroxide spin probes [23] and excited-state resonance Raman spectroscopy [24]. Once the negatively-charged head groups of the surfactant molecules show the same charge than those of carboxylic group of CAHP, it is expected that the hydrocarbon chains of the surfactant ions can be adsorbed by the hydrophobic structure of CAB in order to reduce the free energy of the system, and consequently a HM formation occurs (Fig. 3a).

Having shown that surfactant adsorption increases hydrophobicity of the membranes, the following step was to evaluate how this can affect the blend transport properties, especially in terms of the permeation features.

Support for membrane modification comes from studies of the kinetics of water desorption from the blend (Fig. 2). Both, the rate and mechanism of water desorption show differences in the presence and absence of SDS, showing that the SDS (10 mM) alters the membrane. The effective water diffusion coefficient, D_{weff}, for short-range times [25], as obtained by desorption measurements, decreases from 1.2 (±0.2)×10^{-11} m^2 s^{-1} (without SDS) to 1.3 (±0.2)×10^{-13} m^2 s^{-1}, in the presence of SDS solution. The water concentration in blend C_w decreases from approximately 20% (w/w) to
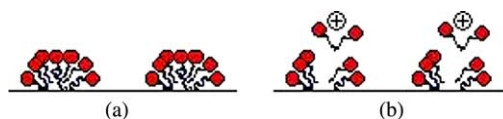

Fig. 3. Schematic representation of hemimicelle formation on the blend surface without (a) and with (b) HCl.

approximately 16% (w/w) when in contact with SDS solution as a direct consequence of the increase in hydrophobicity. The shape of such a kinetic plot also shows at $1 - C_{wt}/C_{w\infty} > 0.6$ a deviation from Fickian behaviour (dashed line in Fig. 2). A possible explanation for such non-Fickian behaviour, with a negative deviation from the theoretical curve, can be due to the occurrence of relaxation phenomena [26] of the polymeric matrix during water desorption. This hypothesis is based on experimental findings of rehological studies of surfactant-urethane ethoxylated hydrophobically modified systems [27].

Since the proposed interaction mechanism of HM formation between SDS and the polymer suggests that an additional resistance to the SDS permeation will occur [28], an estimation of the thickness of such layer was attempted. The analysis of the Fig. 4 shows an unusual increase of SDS flux (J_{SDS}) with an increase of the membrane thickness (l). This behaviour shows that blend features, such as the polar groups of the CAHP as well as the amphiphilic properties of the cellulose structure [13,29,30], are also very important and cannot be neglected in the overall diffusion process analysis. For example, although the cellulose ester membrane shows
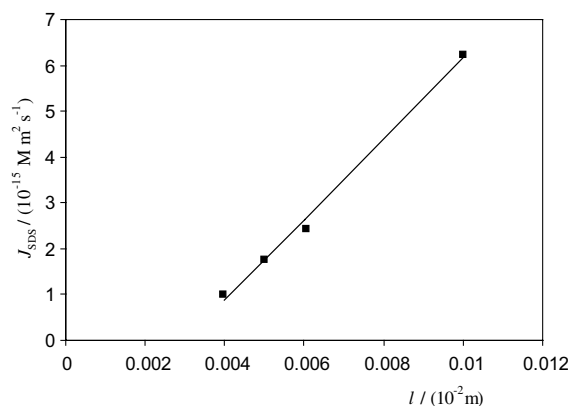
zones with different degrees of crystallinity, the surface presents pores and rough zones, and the bulk of the film does not show any large pores [31], the spongy structure of cellulose derivatives [32] might play an important role in diffusion processes.

A critical discussion of the balance effect between the different properties mentioned on the permeation of SDS and/or HCl will be presented in the next sections.

3.2. Sorption isotherms of SDS

The equilibrium sorption concentrations of SDS, C_{SDS}, in CAB/CAHP membranes at different pH conditions are shown in Table 1. The concentration of the SDS increases with the equilibrium HCl concentration in the system, showing that the sorption of the SDS unimer form increases as a consequence of a decrease in the SDS association, which can be provoked either by the presence of hydrogen ions or of the sulfate groups of SDS hemimicelles (Fig. 3). In the absence of HCl, only a slight increase in C_{SDS} is found with c, noticeably at concentrations near or above the critical micelle concentration (cmc $= 8.16 \times 10^{-3}$ M [33]). The sorption of SDS can occur by two different mechanisms via unimer and/or by interaction between the hydrophobic part of blend and the SDS with consequent hemimicelle formation. The latter mechanism is supported by the high distribution coefficients, observed particularly at SDS concentrations below 1×10^{-2} M. The sorption (by partition) of unimer by the polymeric matrix results from the fact that SDS can permeate the blend membrane only in the unimer form. Confirmation of this has come from studies of permeation across polymer membranes carried out using the fluorescence of pyrene incorporated in aqueous SDS solutions at concentrations above the cmc. After 168 h following the beginning of the permeation experiment there are no indications of pyrene fluorescence in the solution in water cell, confirming that micelles do not permeate the polymer membrane. As a consequence, the results in Table 1 suggest that micelles may act by influencing the entrance of the unimers into membrane.

Fig. 4. Effect of membrane thickness, l, of CAB/CAHP blend membrane on the flux, J_{SDS} of SDS 10 mM in the first 2 days of experiments in steady-state conditions.

Table 1
Equilibrium sorption of SDS aqueous solutions by the CAB/CAHP blend at different HCl concentrations, at 25 °C

c_{SDS}/M	C_{SDS}/M			
	$c_{HCl}(s) = 0$ M	$c_{HCl}(s) = 0.001$ M	$c_{HCl}(s) = 0.01$ M	$c_{HCl}(s) = 0.1$ M
0.001	0.025 (0.002)	0.071 (0.002)	0.128 (0.003)	0.208 (0.003)
0.005	0.025 (0.002)	0.086 (0.003)	0.187 (0.002)	0.235 (0.004)
0.01	0.026 (0.002)	0.091 (0.005)	0.211 (0.005)	0.255 (0.005)
0.05	0.038 (0.002)	0.135 (0.006)	0.316 (0.003)	0.375 (0.002)
0.1	0.051 (0.003)	0.181 (0.006)	0.432 (0.003)	0.535 (0.004)

s—standard deviation of, at least, three independent measurements.

A dual mode isotherm is found to reasonably explain the SDS sorption: in a presence of HCl the SDS concentration tends towards the limit of Henry's law, showing that the permeation of SDS is clearly dependent both on solubility and on the mobile fraction of the sorbed molecules (Eq. (5))

$$C_{SDS} = K'c_{SDS} + K'_0 \tag{5}$$

where K' and K'_0 are constants related with the Henry's law dissolution and site saturation concentration, respectively. If we assume the sorption isotherms of SDS are part of a dual mode sorption then $K'_0 = C_\infty$. The values of K', obtained from fitting the experimental data (Table 1) to Eq. (5), are the following: K'(HCl, 0 M) = 0.27(±0.01), K'(HCl, 0.001 M) = 1.06(±0.07), K'(HCl, 0.01 M) = 2.79(±0.32) and K'(HCl, 0.1 M) = 3.15(±0.43). These results show that the SDS dissolution inside polymeric matrix increases when HCl concentration also increases.

3.3. Sorption isotherms of HCl

The results of HCl sorption by the blend material (Fig. 5), either from aqueous solution or from HCl–SDS mixture, can be reasonably treated in terms of a Langmuir type isotherm (Eq. (6)),

$$C_{im} = K_1 C_\infty C_f / (1 + K_1 C_f) \tag{6}$$

where C_{im} is the concentration of the immobilised sorbed molecules, C_∞ is the concentration of the sorbed molecules which can interact with the polymer, and K_1 is an equilibrium constant involving the sorption and desorption processes. The concentration of free molecules inside polymer, C_f, is assumed to be linked to the concentration in the bulk solution, c, through a Henry's law type equation
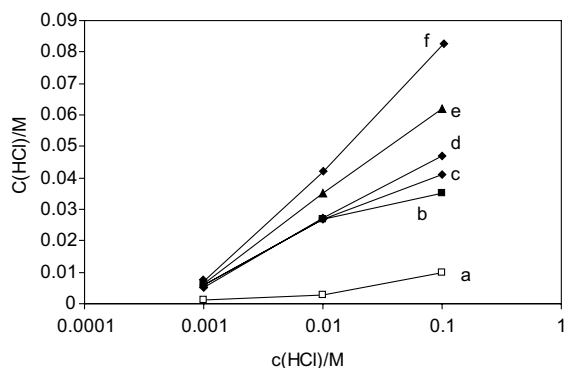

Fig. 5. Dependence of the HCl concentration inside polymeric membrane, C, on the HCl bulk solution concentration, c, in the presence of SDS at different concentrations: (a) 0 M; (b) 0.001 M; (c) 0.005 M; (d) 0.01 M; (e) 0.05 M; (f) 0.1 M. The lines are only to guide the eyes.

Table 2
Langmuir isotherm parameters computed from fitting Eq. (8) to the experimental data shown in sorption isotherms of HCl (Fig. 5)

c_{SDS}/M	K_2	C_∞/M	R^{2a}
0	287	0.0053	1.00
0.001	213	0.034	1.00
0.005	190	0.037	0.99
0.01	128	0.043	1.00
0.05	114	0.063	1.00
0.1	90	0.086	1.00

[a] R^2—correlation coefficient.

$$C_f = K_0 c \tag{7}$$

where K_0 is a partition coefficient. Following Eqs. (6) and (7), Eq. (8) represents the above dependence in terms of reciprocal co-ordinates,

$$1/C_{im} = 1/C_\infty + [1/(K_2 C_\infty)](1/c) \tag{8}$$

where $K_2 = K_0 K_1$.

Table 2 presents the parameters of HCl sorption by polymer blend. The experimental data show an excellent fit to Eq. (8). From these results, and taking into account the experimental results of SDS sorption isotherms, shown in previous section, the following conclusions can be drawn:

- The sorption of HCl by the polymeric structure shows a very low C_∞, indicating that only a small part of the acid interact with the carboxylic groups of the blend.
- As the SDS concentration increases, the formation of hemimicelles increases; under these circumstances the hydrogen ions will interact with the SDS-sulfate group, decreasing the SDS aggregation and increasing the hydrophilicity of polymer.
- As a consequence, the amount of SDS unimers which may go in the polymeric matrix will increase, and the unimer–unimer interactions will become stronger at higher SDS concentrations.
- An increase in the SDS concentration clearly results in a decrease in the rate constant for HCl sorption, supporting the assumption that SDS molecules may compete with HCl for interaction with polymer groups.

3.4. Transport of hydrochloric acid

Permeation experiments on HCl in the polymer membranes show that a steady-state flux is reached within the first 11 h of the experiment and is maintained during 2 days.

However, in the presence of aqueous solutions of SDS, we have shown that there is an alteration of the cellulose

ester membrane structure, and we suspect that the contact between HCl and the polymer blend will be followed by some specific interaction between, for example, the hydrogen ions and the carboxylic groups of CAHP. Such an interaction may result either in a complete immobilization of a fraction of diffusant molecules or their participation in processes leading to their binding to certain sites in the polymeric matrix. Even in the absence of any other complicating circumstances, the effective diffusion coefficients will depend on the rate constants of these reactions.

Assuming immobilisation of free HCl molecules

$$C = C_f + C_{im} \qquad (9)$$

where C is the total concentration, C_f is the concentration of free molecules, C_{im} is the concentration of immobilised molecules ($C_{im} \neq 0$), we can write the flux of this species as

$$J = -D\partial C_f/\partial x = -D_{eff}\partial^2 C/\partial x^2$$

and deduce an effective diffusion coefficient

$$D_{eff} = D(\partial C/\partial C_f)^{-1} \qquad (10)$$

If the concentrations of mobile and immobile molecules are directly proportional ($C_{im} = KC_f$), then the effective diffusion coefficients remain constant: $D_{eff} = [D/(1+K)]$. If we assume a limited number of specific sites (as, for example, in the Langmuir mechanism of sorption), D_{eff} will increase with concentration of diffusing species, with values approaching diffusion coefficient of free molecules. Using membranes of 0.040-mm thickness, the D_{eff}, for HCl 0.001, 0.01 and 0.1 M, are 0.71×10^{-14}, 3.0×10^{-14} and 4.8×10^{-14} m^2 s^{-1}, respectively.

The diffusion coefficient D of HCl in CAB/CAHP blend at $C_{SDS} = 0$ can be calculated using the parameters from the Langmuir sorption calculated above and the effective diffusion coefficients D_{eff}. Using the derivative ($\partial C/\partial C_f$) from Eqs. (6) and (10), we obtain

$$D = D_{eff}\left(K_0 + K_1 C/(1+K'c)^2\right) \qquad (11)$$

The diffusion coefficient calculated using Eq. (11) is $D = 4.92 \times 10^{-14}$ m^2 s^{-1}, and shows a high resistance of the blend to the transport of HCl. From Eq. (11) we can also calculate K_0 (= 0.15), showing that a small part of the sorbed molecules are free to diffuse.

3.5. Diffusion of SDS at different HCl concentrations

Analysis of SDS permeation in the HCl mixtures are not easy to interpret, particularly when we are working with a quaternary system. Such analysis is further complicated by other phenomena such as aggregation equilibrium between monomers and micelles, at SDS concentrations above cmc and possible chemical reactions between some of the species in solution. Taking into account such difficulties, and once the SDS flux through the polymer blend was obtained in an independent form, we have decided to describe the permeability of SDS in terms of a simple diffusion process

$$\partial C/\partial t = \partial/\partial x(D_F\partial C/\partial x) \qquad (12)$$

with the boundary and initial conditions $C(0,t) = C_{SDS}$, $C(l,t) = 0$, (where C_{SDS} is the concentration of the surfactant in the membrane) and $C(x,0) = 0$, resulting in the simple formulae for calculation of the permeability (P_S) and apparent diffusion (D_F) coefficients [11]

$$P_S = J_{SDS}l/c_{SDS} \qquad (13)$$

$$D_F = l^2/6\theta \qquad (14)$$

where J_{SDS} is the steady-state flux of SDS through the membrane, θ is its time-lag, and c_{SDS} is the bulk concentration of the SDS.

As pointed out earlier, fluorescence measurements in permeation experiments of SDS at concentrations above the cmc have shown that the diffusing species permeating the polymer membranes are only surfactant monomers. As a consequence, the apparent diffusion coefficient is that due to the monomer ($D_F = D_m$). This also shows that, at $c_{SDS} >$ cmc, Eq. (14) can be rewritten as

$$P_S = J_{SDS}l/[SDS]_{cmc} \qquad (15)$$

The critical micelle concentration used in Eq. (15) is $[SDS]_{cmc} = 8.16 \times 10^{-3}$ M [33]. Table 3 shows the flux (J_{SDS}), permeability (P_S) and apparent diffusion (D_m) coefficients of SDS through a CAB/CAHP blend, at different HCl concentrations.

The flux of SDS through polymeric blend increases with SDS concentration showing that the SDS concentration inside polymer is an important factor in this process. We can also observe, from Table 2, that J_{SDS} clearly increase when the HCl concentration also increase (for example, $J_{SDS=0.1\,M}$ (HCl = 0 M) = 0.82×10^{-7} mol m^{-2} s^{-1} and $J_{SDS=0.1\,M}$ (HCl = 0.1 M) = 4.61×10^{-7} mol m^{-2} s^{-1}), showing that the SDS amount free to move inside the blend matrix also increased. It also possible to conclude that the J_{SDS} show two distinct rates of permeation (dJ_{SDS}/dc_{SDS}): one relatively high at the low SDS concentrations (for example, at $c_{HCl} = 0$, dJ_{SDS}/d$c_{SDS} = 11.07 \times 10^{-10}$ m s^{-1}) and the other relatively low at SDS concentrations higher than 0.01 M (for example, at $c_{HCl} = 0$, dJ_{SDS}/d$c_{SDS} = 2.402 \times 10^{-10}$ m s^{-1}). The intersecting point of these two distinct rates is approximately 0.010 M (very close to the SDS cmc), showing that the faster flux is due to the unimers, and the slower flux is due to the presence of micelles which can also favour new kinds of interactions, particularly those between these new entities and the non-polar structure of the cellulose-based blend [34].

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Table 3
Flux, J_{SDS} permeability, P_S, and apparent diffusion, D_m, coefficients of SDS through CAB/CAHP blend membranes at different HCl concentrations at 25 °C

c_{SDS}/M	c_{HCl} = 0 M			c_{HCl} = 0.001 M			c_{HCl} = 0.01 M			c_{HCl} = 0.1 M		
	J_{SDS}/(10^{-7} mol m^{-2} s^{-1})	P_S/(10^{-13} m^2 s^{-1})	D_m/(10^{-12} m^2 s^{-1})	J_{SDS}/(10^{-7} mol m^{-2} s^{-1})	P_S/(10^{-13} m^2 s^{-1})	D_m/(10^{-12} m^2 s^{-1})	J_{SDS}/(10^{-7} mol m^{-2} s^{-1})	P_S/(10^{-13} m^2 s^{-1})	D_m/(10^{-12} m^2 s^{-1})	J_{SDS}/(10^{-7} mol m^{-2} s^{-1})	P_S/(10^{-13} m^2 s^{-1})	D_m/(10^{-12} m^2 s^{-1})
0.001	0.50 (0.03)	8.43	6.2	0.38 (0.03)	7.90	6.2	0.45 (0.03)	7.43	7.1	1.53 (0.05)	27.5	10.1
0.005	0.55 (0.02)	2.09	6.4	0.52 (0.01)	2.13	6.9	0.41 (0.02)	1.97	8.9	2.28 (0.04)	8.21	13.0
0.01	0.60 (0.03)	1.40	6.6	0.62 (0.02)	1.48	7.6	0.68 (0.03)	1.83	10.2	3.31 (0.02)	7.71	15.4
0.05	0.75 (0.03)	1.65	6.7	0.68 (0.02)	1.71	7.9	0.87 (0.02)	2.24	10.8	3.98 (0.03)	8.78	15.2
0.1	0.82 (0.04)	1.81	7.0	0.72 (0.03)	1.81	8.0	1.03 (0.04)	2.52	11.0	4.61 (0.05)	10.2	15.1

From the analysis of the P_S values we may remark: (a) at c_{SDS} < cmc the permeability coefficients decrease with an increase of SDS concentration; (b) at c_{SDS} > cmc a slight increase in P_S is found. The first fact can be explained by the formation of hemimicelles which act as a further resistance to the whole SDS flux; the latter finding shows that although micelles do not permeate the membrane, they do produce an extra contributing factor to driving force of monomer diffusion. This occurs because it seems that at c_{SDS} > cmc the HM formation reaches the saturation point. The presence of HCl only becomes significant to P_S at concentrations higher or equal to 10^{-2} M; at this concentration the effect on P_S is only found at concentrations above cmc, whilst at 0.1 M HCl conditions a drastic increase of P_S occurs. These results also show that, although the effect of HM cannot be neglected, its effect decreases with the SDS association which is induced by the presence of HCl.

The analysis of the apparent diffusion coefficients shows that in the absence of HCl almost no variation of D_m with concentration is observed, supporting the assumption that the monomer species are the only significant free diffusing species inside the membrane. As HCl concentration increases, the variation of D_m, as a function of c_{SDS}, increases too, in a significant way at c_{SDS} < cmc, showing that the resistance to the hydrodynamic flux decreases with an increase of free monomers; another possible explanation arises from a possible drag effect produced by the hydrogen ions. However at higher SDS concentrations, D_m values become approximately constant also showing that the micelles do not have a relevant role in the diffusion process.

4. Conclusions

The sorption of SDS on cellulose ester blend membranes occurs via hemimicelle formation in accordance with high distribution coefficients and increase in hydrophobicity of the surface as seen by fluorescence. Such an increase in the blend hydrophobicity leads to a consequent decrease in the water diffusion coefficient and in the permeability coefficient of the unimer. This occurs specially at concentrations where only unimer species exist; when micelles exist in solution, a small increase in the permeation is found, showing that the variation of this parameter depends on the cmc. The analysis of the apparent diffusion coefficient leads to values approximately two orders of magnitude lower than in aqueous solution, showing that although the concentration of free diffusing unimers increases with concentration, the concentration tends to be very small. The spongy structure of cellulose as well as the presence of the polar groups of CAHP are suggested to be very important to mass transport by diffusion. It is known that the presence of hydrophilic groups, even in very small concen-

tration, may control the diffusion process. This is suggested to be true also for the blend studied, even though the hydrophobic character of this is increased by formation of the SDS hemimicelles.

The hydrophilic/hydrophobic balance in the blend as well its effect on the transport properties of SDS can be modified by changing the HCl concentration. This may be used as an important tool to control the permeation of solutes through this kind of membranes. An increase of P_S and D_m is clearly found when pH increases, showing that SDS permeation can be controlled by altering the acidic concentration in the bulk solution, once the hydrogen ions will interact with the SDS, decreasing their association, and consequently changing the membrane properties.

Although the reported experimental results are not easy to interpret, we suggest a mechanism of transport and equilibrium involving the following steps: (i) the surfactant approaches the polymeric surface; (ii) hemimicelle formation occurs on the hydrophobic part of the blend, and, as a consequence, the polymeric membrane changes to have a more hydrophobic character; (iii) after a certain period of time all the ionic (hydrogen phthalate) and cellulose sites of the polymeric blend (both at the surface and most probably inside the polymer membrane) will be completely occupied, such that a "new" surface modified polymeric blend can be considered to exist, and to be accompanied by a relaxation of the membrane structure; (iv) in the presence of the acidic solute a synergetic mechanism may be involved: with the protonation of carboxylic groups, the HCl is available to decrease the SDS association and, as a consequence, the concentration of SDS which can dissolve inside the blend and diffuse will increase.

More experimental work is in progress to finally characterise this blend system. However, the present and previously reported experimental results show that such a matrix seems to have very promising features for use in separation processes since its dependence on hydrophobic/hydrophilic balance can be enhanced by the presence of SDS, and transport properties can be modulated by changing the acidity of the bulk solution.

Acknowledgements

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