Diffusion and Sorption Studies of Dyes Through PVA Cryogel Membranes

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ABSTRACT: The capacity of poly(vinyl alcohol) (PVA) to crosslink through freeze/thaw method was used to obtain PVA hydrogel membranes (HG) that were subjected to sorption and diffusion experiments using three dyes: Congo red (CR), methylthymol blue (MTB), and crystal violet (CV). To study the sorption of dyes into the cryogenic membrane, dye solutions at different concentrations were used. After sorption, desorption of dyes from the PVA membrane was monitored to quantify the possible regeneration of the membrane (PVA HG). To have a deep insight on the mechanism behind the desorption process, dye-release kinetics were studied. The diffusion experiments reveal the fact that CR and MTB do not permeate the PVA HG membrane making it a promising candidate in the advanced purification processes of wastewaters. The effect of the incorporation of dyes (CV, CR, and MTB) on the chemical properties of PVA cryogel matrices has been studied by using several techniques such as: differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1445–1453, 2010

Key words: hydrogel; dyes; diffusion; membrane

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a polymer of great interest because of its many desirable characteristics, specifically for various pharmaceutical, biomedical, and separation applications.[1]

Dye-doped polymer films have been studied for many applications, including optical waveguides,[2] polymeric solid-state lasers,[3] optical amplifiers,[4] and optical storage media.[5] PVA has also been used as a matrix for dye-containing nonlinear optical materials due to its unique properties such as low cost, readily available, easily processable, and biocompatibility. For example, Congo red (CR) and crystal violet (CV)-doped PVA have been shown to exhibit strong optical limiting behavior.[6,7] PVA has also been used as a solid matrix for physical[8] or chemical[9] incorporation of fluorescent dyes. PVA-dye systems can also be used for coating nanoparticles to improve the nanoparticles catalytic activity.[10,11] Another important application of PVA is its use for discoloration of dye-containing wastewaters.[12–15]

In this article, we report the equilibrium (sorption and desorption isotherms) and transport (diffusion and permeability coefficients) properties of a set of dyes (CV, MTB, and CR) through physical crosslinked PVA hydrogel membranes (HG). PVA gels can be prepared by chemical or physical crosslinking; general methods for chemical crosslinking are the use of chemical crosslinkers or the use of electron beam or γ-radiation, whereas the most common method to produce physical crosslinking PVA is the so-called "freezing-thawing" process.[1] The formation of a gel network by physical crosslinks can be mainly explained by the formation of hydrogen bonds and crystallites. These physically crosslinked gels exhibit higher mechanical strength than PVA gels crosslinked by chemical or irradiative techniques, because the mechanical load can be distributed along the crystallites of the three-dimensional structure.[1] The "freezing-thawing" method addresses toxicity issues because it does not require the presence of a crosslinking agent and, consequently, no toxicity agents are leaching out from the gel matrix. Some characteristics of these "physically" crosslinked PVA gels include a high degree of swelling in water, a rubbery and elastic nature, and a high mechanical strength. In addition, the properties of the gel may depend on the molecular weight of the polymer, the concentration of the aqueous PVA solution, the temperature and time of freezing and thawing, and the number of freezing/thawing cycles.[16,17]

MATERIALS AND METHODS

Materials and membrane preparation

PVA industrial grade (polymerization degree ~ 900; hydrolysis degree 98 mol %; polydisperse) was

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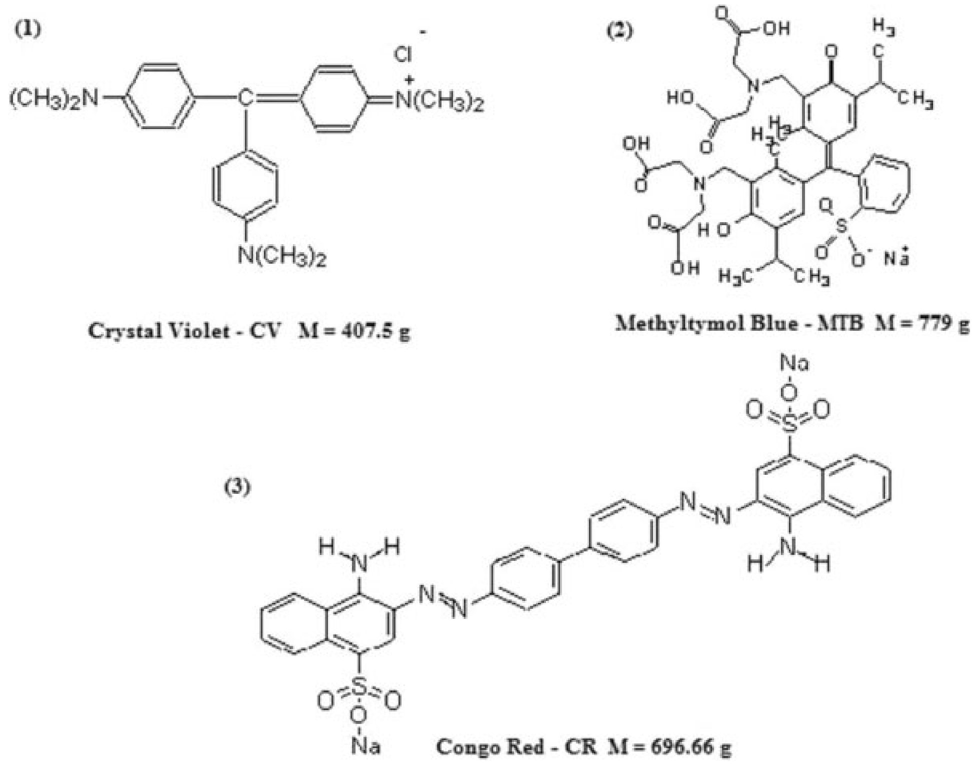


Crystal Violet - CV M = 407.5 g

Methyltymol Blue - MTB M = 779 g

Congo Red - CR M = 696.66 g

Figure 1 Chemical structures of CV (1), MTB (2), and CR (3).

acquired from Chimica Râşnov—Romania and used as received.

Three different dyes (Fig. 1) have been used in this work: CV, purchased from Fluka, is an azo dye with two azoic groups in its structure (—N=N—) and triarylmethane dyes CR and MTB, both were purchased from Merck. All reagents were used without further purification. All solutions were prepared by dissolving the specific amount of the compound in distilled water. Sodium chloride proanalysis (Merck) was also used without further purification.

The PVA cryogel membranes were prepared as follows[18]: a PVA solution of 14 wt % concentration was prepared by dissolving a certain amount of PVA into distilled water at 80°C under continuous stirring for 3 h. After mixing, 10 mL of solution were cast in Petri boxes and submitted to freezing for 12 h at −20°C and, after that, thawed for 12 h at +25°C. The cycles of freezing and thawing were repeated three times. After that, strong thermoreversible PVA hydrogel (PVA HG) membranes exhibiting mechanical integrity and a white and opaque appearance caused by a heterogeneous structure were obtained.[19] They were kept in distilled water for later use (not longer than 6 months). The obtained membranes have a thickness of around 1.00 mm, as measured by a Mitutoyo digimatic micrometer (±0.001 mm), and a hydration (mass of water in the swollen gel/mass of swollen gel) of 0.89.

PVA membranes characterization

SEM measurements

The surface morphology of PVA membranes has been analyzed by SEM with a JSM-5130 scanning microscope operating under low vacuum at 25 kV.

The membranes were previously dried in a Labconco Freeze Dryer 4.5. Previously, the samples were frozen in liquid nitrogen at $T = -196°C$ for about 30 s. Before examination, the samples were coated with a thin layer of gold and palladium.

Differential scanning calorimetry measurements

Differential scanning calorimetry (DSC) tests were carried out on a Diamond DSC Heat Flow PerkinElmer, using about 10 mg of each sample at a heating rate of 5°C/min from 20°C to 250°C, and then cooled with the same rate for three cycles.

Fourier transform infrared measurements

The incorporation of dyes into PVA gel membranes was characterized by their infrared spectra using a Fourier transform infrared (FTIR) PerkinElmer spectrometer with ATR device. The FTIR spectra were recorded on the gel membranes as they were obtained.

Permeation studies

The permeation experiments have been carried out as follows: the diffusion cell has two compartments with a volume V of 250 mL, A the donor compartment and B the receptor compartment, interconnected through an opening of 0.659 cm^2 area (A). The PVA membrane, with a thickness l (where l values were between 0.75 mm and 1.2 mm), previously swollen in water, was placed between the two compartments. The diffusion cell was placed under a magnetic stirrer F20 FALC, so that in both compartments there was continuous stirring. To determine the amount of diffused dye that permeates the membrane, every 4 min, 4 mL of sample were extracted from B compartment. The diffusion cell temperature was kept at 25°C using a Velp Sientifica thermostatic bath. The solutions were analyzed using visible absorption spectroscopy on a UV–VIS Jasco V-530; on the basis of these measurements, the flux of dyes through the PVA membrane was determined and, consequently, the integral diffusion, D_θ, and the permeation, P, coefficients were calculated[20] by the following equations:

$$D_\theta = \frac{l^2}{6\theta} \tag{1}$$

$$P = \frac{Vl}{Ac_i}\frac{dc}{dt} \tag{2}$$

where l is the membrane thickness, θ is the time-lag, t is the time, dc/dt is the dye permeation rate and c_i ($=1 \times 10^{-4}$ M) is the initial concentration of aqueous dye solution in the feed compartment (cell A).

Sorption/desorption studies

To study the sorption of dyes into the cryogenic membrane, dye solutions at different concentrations were used. For each dye, the concentration range considered was selected taking into account the solubility of dyes in water (1.68 g CV < 3.3 g CR < 10 g MTB/100 mL water). During the dye sorption process, the PVA membranes change their color from white to: red for CR sorption, blue for CV sorption and light brown for MTB sorption but they remain stable during the sorption/desorption process.

A Velp Sientifica thermostatic bath was used to keep the solutions temperature during sorption/desorption experiments at 25.0°C (±0.1).

The amount of the dye sorbed by PVA membrane was determined by monitoring the concentration of the dye solution through visible spectroscopy using an UV–VIS Jasco V-530 spectrometer at 400–700 nm. The sorption was monitored in a daily basis and the equilibrium of sorption was reached after 20 days.

The concentration of the dye sorbed by the membrane, C_{ss}, was calculated using

$$C_{ss} = (c_i - c_\infty)V'/(\text{polymer volume or mass}) \tag{3}$$

by measuring the concentration of the sorbed species in aqueous solution of a volume V' prior (c_i) and after (c_∞) the sorption experiments, using the absorbance at the following wavelengths: $\lambda_{MTB} = 440$ nm, $\lambda_{CR} = 498$ nm, and $\lambda_{CV} = 590$ nm.

The desorption of dyes from the PVA membrane was monitored to quantify the possible regeneration of the membrane (PVA HG). Initially, PVA membranes were immersed in dye solution and left to reach the equilibrium. After this equilibrium time, the PVA membranes were removed, the excess of solution was wiped off, and the membranes were immersed in a given volume of distilled water. The dye desorption was monitored by UV–VIS spectroscopy.

In MTB case, the desorption could not be followed at the specific wavelength $\lambda_{MTB} = 440$ nm.

RESULTS AND DISCUSSIONS

Chemical characterization of PVA-dye gels

DSC analysis

The effect of the incorporation of dyes (CV, CR, and MTB) on the chemical properties of PVA cryogel matrices has been studied by using several techniques. The thermal analysis of those gels was carried out by DSC. For all gels, it is possible to observe well-defined endothermic transitions in a temperature range between 200 and 240°C, corresponding to the melting of the PVA crystals.[21] The PVA shows a melting temperature (T_m) at 225°C, in agreement with the literature.[21] The presence of CV and MTB leads to a slightly increase of the T_m of the composite gel (T_m = 227.4 and 229.2°C, respectively). However, there is a significant decrease of the T_m, to 218°C, for the PVA/CR composite gel (Fig. 2). In a first approach, it is possible to conclude that the addition of CR to the PVA determines a lack of PVA crystallinity. To gain a deep insight on the effect of dyes on the structure of PVA and PVA-composite gels, a thermodynamic analysis was carried out, and enthalpies of melting, ΔH_m were calculated. Table I shows the effect of loaded dyes on ΔH_m and on the crystallinity degree (CD). CDs were calculated as the ratio between the enthalpy of melting (ΔH_m) of the PVA or PVA-composite and the enthalpy of melting of the polymer in its completely crystalline state (ΔH_m^o),[22] which for PVA is 138.6 J/g.[23] It is possible to conclude that the PVA structure has a significant loss of crystallinity (approximately 50%) when loaded with CR. The decrease of the heat of melting

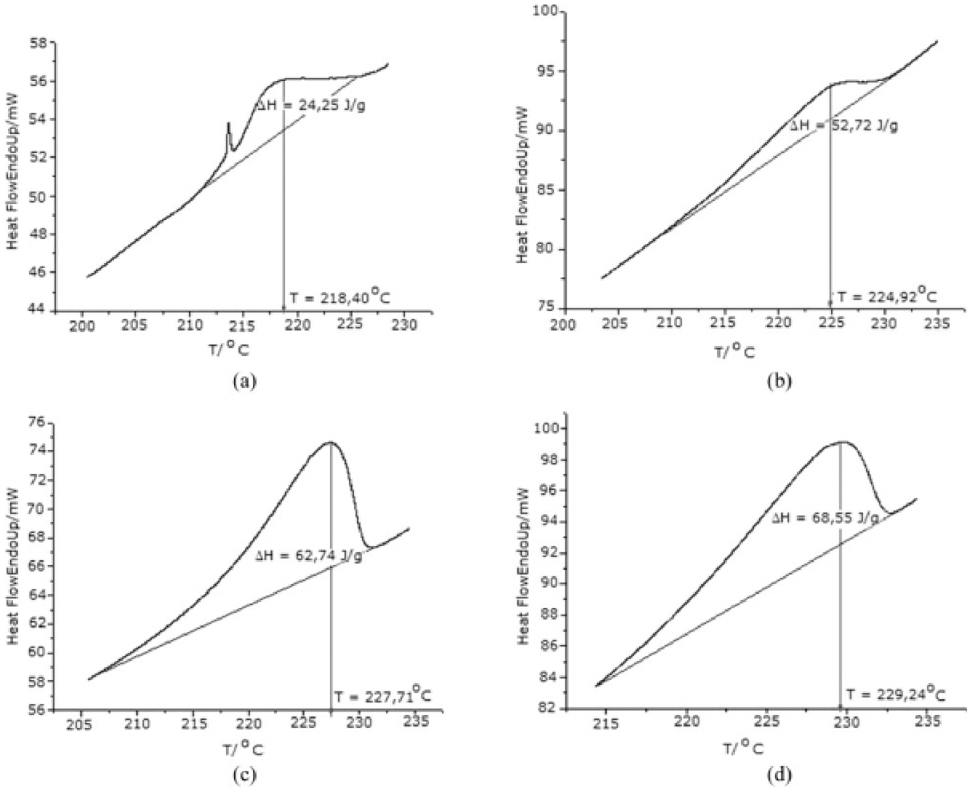


Figure 2 DSC diagrams for (a) PVA/CR, (b) PVA, (c) PVA/CV, and (d) PVA/MTB.

for PVA/CR composite can be justified by a chemical interaction of CR, acting as crosslinker, with the PVA structure, via formation of hydrogen bonds between hydroxyl groups of PVA and amino and/or azo groups of CR.[24] Park et al.[25] have suggested that the addition of crosslinker molecules to PVA will attenuate the degree of crystallinity and, consequently, enthalpy of melting decreases. Furthermore, the high ability of CR to suffer dissociation in aqueous solution can also contributes to such decrease in the CD.[26]

The incorporation of CV and MTB inside PVA matrix has an opposite effect on ΔH_m and T_m values, when compared with the CR; that is, there is an increase of both melting temperature and crystallization degree in those composite PVA-based gels. We can hypothesize that the presence of those dyes inside of PVA matrix will lead to a slight structuring effect on the PVA chains, by increasing the PVA–PVA interactions (through hydrogen bonds between the polymeric chains) and thus increasing the crystallinity of the gel structure.

FTIR analysis

The effect of dyes on the PVA structure has also been analyzed by FTIR (Fig. 3). In all spectra, it is possible to observe characteristic absorption bands of PVA at 3283 cm^{-1} and 2924 cm^{-1}, assigned to hydrogen bonds from —OH groups and to the stretching vibrations of alkyl groups (C—H), respectively.[27,28] Comparing the FTIR spectra of dye-PVA composite gels with that of PVA, no additional, or shifted, vibration bands are observed. This clearly suggests that no new covalent bonds, between PVA and dye, are formed.

The vibrational band at $\upsilon_2 = 1090$ cm^{-1}, assigned to the C—O stretching band, is usually related to the PVA crystallinity, and it is interpreted in terms of the formation of intra- and intermolecular hydrogen bonding among PVA chains due to strong hydrophilic forces.[29] Furthermore, the vibrational band at $\breve{\upsilon}_1 = 1140$ cm^{-1} is assigned to the crystalline fraction of the PVA membrane. The ratio of the heights of the vibrational peaks $\acute{\breve{\upsilon}}_1$ and $\acute{\breve{\upsilon}}_2$, h_1 and h_2, respectively (Table II), will allow us to obtain a comparative assessment of the effect of a dye on the CD of the gel membrane.[30] By comparing the ratio h_1/h_2 values, which can give a qualitative measure of the

TABLE I
CD for the PVA and PVA Membranes Loaded with Dyes

	PVA	PVA/CR	PVA/CV	PVA/MTB
ΔH_f [J/g]	52.7	24.2	62.7	68.6
CD (%)	38.0	17.5	45.3	49.5

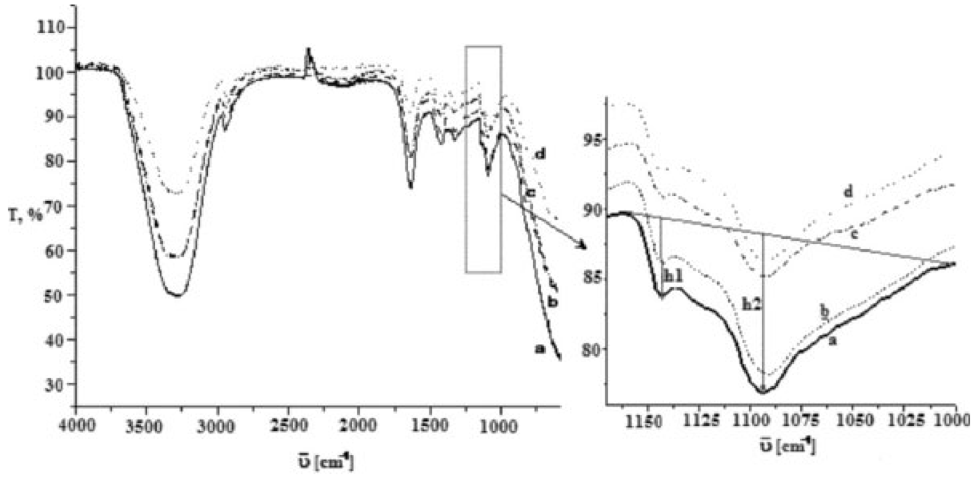


Figure 3 FTIR spectra for (a) PVA, (b) PVA/CV, (c) PVA/CR, and (d) PVA/MTB membranes.

PVA crystallinity, we can see that for the PVA membranes loaded with MTB or CV h_1/h_2 is higher, meaning a higher crystallinity of the gel compared with the neat PVA membrane, whereas for the PVA/CR, the ratio value is lower, meaning a lower CD. This trend is in close accordance with the DCS measurements.

SEM study

The effect of dyes on the surface morphology of the PVA-based gels was analyzed by SEM (Fig. 4). The incorporation of CR to the PVA gel leads to a significant increase in the surface porosity; however, in the presence of MTB and CV, it is possible to observe large nonporous featureless areas, suggesting a higher PVA compaction.

Sorption/desorption isotherms

To have a deep insight on the mechanism of interaction between PVA and dyes, sorption isotherms have been measured (Fig. 5). (The following discussion on this issue is only based in the dye concentration range analyzed.)

The sorption isotherm of MTB follows a linear dependency:

$$C_{ss} = K \times c_i \tag{4}$$

where C_{ss} is the dye concentration sorbed by the gel (mol/g of hydrogel) and c_i is the initial dye concentration (mol/L) in the aqueous solution; for MTB the partition coefficient, K, is equal to 16.0 (±0.5) L/g. This behavior gives indication that interactions between MTB and PVA are weaker than intermolecular PVA–PVA interactions. The sorption of CV also follows a linear dependence according to eq. (4), with a K value equal to 23.6 (±0.7) L/g.

However, the sorption isotherm of CR is clearly nonlinear; it suggests that with the increase of the concentration of the CR aqueous solution, a plateau of the sorbed CR concentration is reached. This approach can be mathematically expressed using a Langmuir-type isotherm equation[31]

$$C_{ss} = \frac{C_P K' c_i}{1 + K' c_i} \tag{5}$$

where C_P is the maximum concentration of sorbed molecules, c_i is the equilibrium concentration, and K' is an equilibrium constant involving the sorption and desorption processes. The values of K' and C_P, obtained from fitting the experimental data (Fig. 5) to eq. (5), are the following: $K' = 3.8\ (\pm 0.1)$ L/μmol and $C_P = 20\ (\pm 4)$ μmol/g.

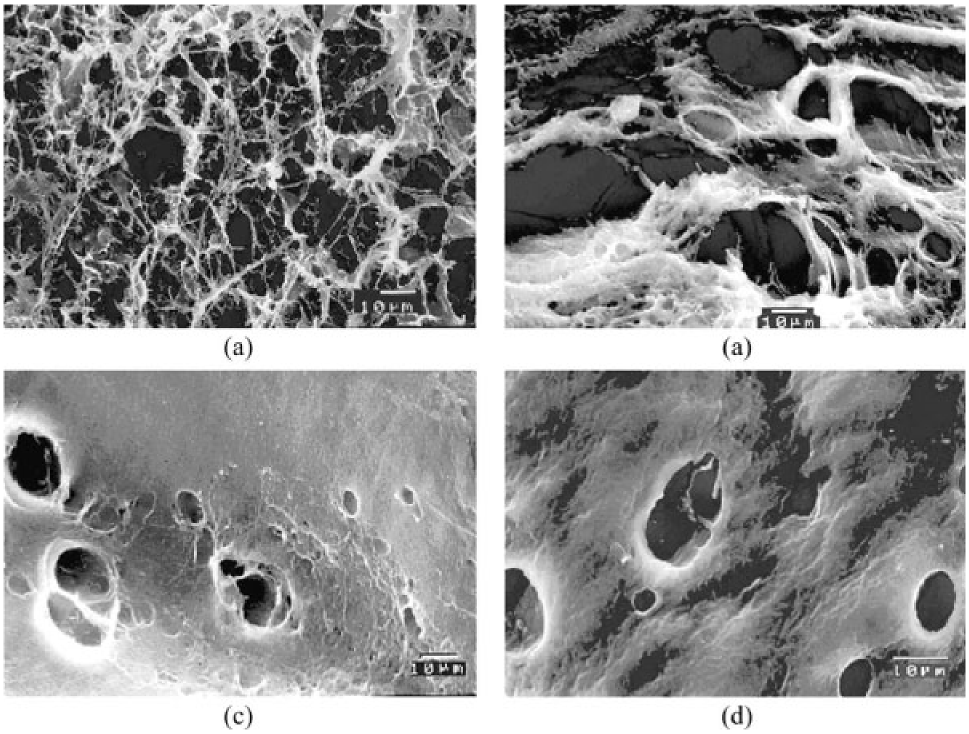
Another interesting parameter that gives information on the sorption equilibrium between PVA and gels is the percentage of dye uptake, given by the following equation as

$$\%\text{dye uptake} = (m_{\text{ss,dye}}/m_{i,\text{dye}}) \times 100 \tag{6}$$

where $m_{\text{ss,dye}}$ is mass of the dye sorbed into the membrane at equilibrium and $m_{\text{i,dye}}$ is the initial mass of the dye in solution. The values of percentage of dye uptake for all dyes are 31%, 58%, and 98% for MTB, CV, and CR, respectively. It is

TABLE II
Comparison Between IR Bands for PVA and PVA/Dye Membranes and Their Ratio

	$\acute{\upsilon}_1$ (cm^{-1})	h_1 (%R)	$\acute{\upsilon}_2$ (cm^{-1})	h_2 (%R)	h_1/h_2
PVA	1144	4.77	1094	10.53	0.453
PVA/CR	1142	3.58	1094	8.40	0.426
PVA/MTB	1142	4.56	1092	9.86	0.462
PVA/CV	1142	5.43	1092	11.92	0.456



(a) (a)

(c) (d)

Figure 4 SEM images of PVA-dye composite membranes. (a) PVA (25 kV, ×750), (b) PVA/CR (25 kV, ×1000), (c) PVA/CV (25 kV, ×1000), and (d) PVA/MTB (25 kV, ×1000).

worthwhile to note that the percentage of dye uptake for different dyes is closely related to the CD of the PVA gel matrix.

To check the effect of the sorption mechanism on the chemical properties of PVA-dye composites, desorption isotherms of CV and CR-PVA gel composites have been obtained. The experimental results are shown in Figure 5 (black points). Comparing the values of sorbed (C_{ss}) and desorbed (C_{ds}) concentrations of dyes, it is possible to conclude that there is a linear relationship between them with a slope (C_{ds}/C_{ss}) of 0.686 (±0.007) and 0.035 (±0.001) for CV and CR, respectively. These values show that CR is highly retained by the PVA matrix when compared with CV; in fact, a large percentage, up to 96%, of sorbed CR remains hold inside the gel matrix. This is in close agreement with the hypothesis that this dye might act as crosslinker of PVA. In the case of CV, there is not so drastic hysteresis between sorption and desorption isotherms, showing a 24% variation for the highest initial CV concentration. The main significance of these values is that although the sorption isotherm can be defined in terms of a linear relationship, the sorption mechanism is not only due to dissolution of dye in the water phase of the PVA gel but also there is a fraction of immobilized dyes. Further support for this comes from the permeability experiments. Generally, with steady-state transport processes through membranes, there is a time-lag (θ) associated with the dissolution of the permeant species to a constant level before the steady state is achieved. In addition, an increase in the induction period may be found with an increase in the interaction between the permeant species and the polymeric matrix.[32] The permeation of CV from 0.1 m*M* initial solution, through PVA membranes leads to a θ equal to 1.8 h followed by a steady-state flux, with a permeability coefficient of 1.6×10^{-10} m^2 s^{-1}. Taking the θ value for a membrane thickness of 750 μm, we find that the integral diffusion coefficient of CV

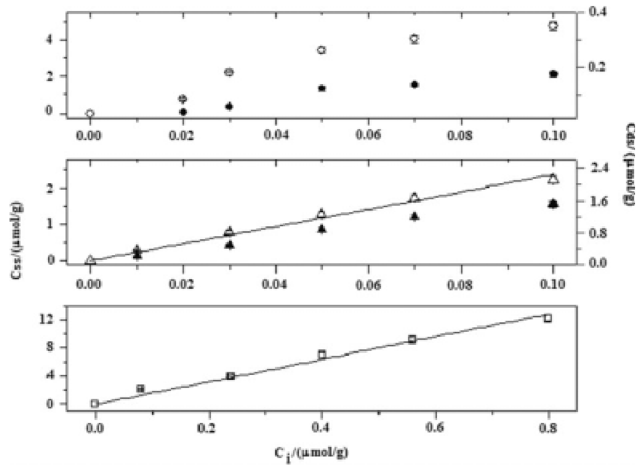


Figure 5 Sorption (white points) and desorption (black points) isotherms of (□) MTB, (Δ) CV, and (○) CR into PVA membranes. The solid lines were obtained by fitting the experimental data using eqs. (4) and (5).

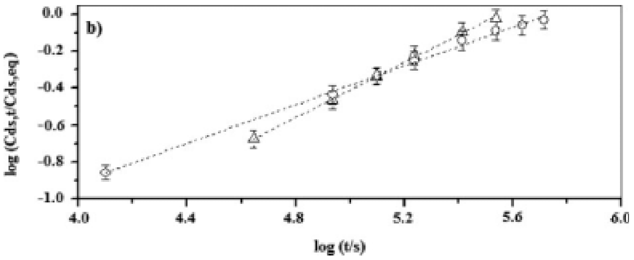


Figure 6 Desorption kinetics of CR (○) and CV (Δ) from PVA gel membranes preequilibrated with dye aqueous solutions of 1–20 μ*M* of dye, respectively. Dashed lines represent the fitting of the experimental data to eq. (7) (see Table III).

is equal to $D_\theta = 1.5 \times 10^{-11}$ m^2 s^{-1}, as calculated by eq. (1). The distribution coefficient obtained by the time-lag technique, K_θ, defined as P/D_θ, gives a value of $K_\theta = 11$, indicating that the PVA matrix has a great affinity to CV dye, as suggested by the partition K obtained by eq. (4).

This diffusion coefficient is 30 times higher than that computed from eq. (9)—see following section. Recently, Cheng and Sun[33] have reported that the use of time-lag method to compute diffusion coefficients of solutes through hydrogels leads to the highest values (sometimes higher than order of magnitude) of diffusion coefficients and is a consequence of a simplistic model that does not describe the physical reality. The integral diffusion coefficient, D_θ, is an averaged overall coefficient for the solutes distributed in the free and the immobilized form during the transport process through gel membrane. Consequently, a more realistic model must take into account the immobilization reaction along with the diffusion[33]; furthermore, the calculus of effective diffusion coefficients through hydrogels must be take into account the volume fraction of the water channels or the porosity of the polymer networks in the hydrogel and the tortuosity of those channels.[34,35] Consequently, further experiments carried out on similar systems must take into account all these further parameters.

Similar experiment has been carried out for a 1 m*M* CR solution and for a 1 m*M* MTB solution; during 515 h, no CR or MTB permeation has been detected by UV–VIS spectroscopy. It is obvious that the very strong interactions between CR and PVA, as suggested by previous discussions, determine the impermeability of the PVA membrane against CR. Concerning the fact that MTB does not permeate the membrane, this is due to the intermolecular PVA–PVA interactions that are stronger than the MTB–PVA interactions and to the increasing crystallinity of the PVA–MTB membrane that hinder the membrane permeation by the MTB molecules.

Desorption kinetics

In the previous section, we have found that dyes do not completely desorb from the PVA matrix. To have a deep insight on the mechanism behind the desorption process, dye-release kinetics were studied. Figure 6 shows representative data of the desorption kinetics plotted in the form of fractional amount of released dye ($C_{\mathrm{ds},t}/C_{\mathrm{ds,eq}}$) as a function of time. The concentration of dye desorbed by the polymer at time t, $C_{\mathrm{ds},t}$, is represented by[36]

$$\frac{C_{\mathrm{ds,t}}}{C_{\mathrm{ds,eq}}} = kt^n \tag{7}$$

where $C_{\mathrm{ds,eq}}$ is the concentration of dye desorbed at the equilibrium, k is a dimensionless constant, and n a parameter related to the diffusion mechanism. If the exponent n is 0.5 (for planar systems), the diffusion is Fickian. Non-Fickian (anomalous) behavior is observed for $0.5 < n < 1.0$, with a limit of Case II transport for $n = 1$.[36]

From the analysis of n values, shown in Table III, we can conclude that the diffusion mechanism of dye release is clearly dependent on the initial dye concentration (c_i). At low initial CV and CR concentrations, the diffusion mechanism is anomalous; however, n approaches to 0.5 for highest CV and CR initial concentrations, giving information that at these conditions the desorption mechanism becomes Fickian. These values suggest that when the sorbed dye concentration decreases (because the abnormal diffusion is a relaxational process and it takes place at low concentration) the polymer relaxation rate is higher than the dye diffusion rate. This is in close agreement with previous discussions; in fact, by

TABLE III
Fitting Parameters of the Logarithm Form of eq. (7) to Experimental Desorption Kinetic Data (see Fig. 5) at Different Initial (c_i) Dye Concentrations

c_i	1 μ*M*		3 μ*M*		5 μ*M*		7 μ*M*		10 μ*M*	
CV	n	k	n	k	n	k	n	k	n	k
	0.77	6×10^{-5}	0.75	1.5×10^{-4}	0.62	8×10^{-4}	0.55	7×10^{-4}	0.50	1.5×10^{-3}
c_i	2 μ*M*		6 μ*M*		10 μ*M*		14 μ*M*		20 μ*M*	
CR	n	k	n	k	n	k	n	k	n	k
	0.63	3×10^{-4}	0.63	3.3×10^{-4}	0.59	4.8×10^{-4}	0.54	9×10^{-4}	0.52	1×10^{-3}

increasing the concentration of sorbed dye, the fraction of free dye also increases and consequently the diffusion process is more dependent on the dye concentration gradient. As a consequence, the diffusion coefficients, D, of CV (for c_i equal to 7 and 10 μM) and CR (for c_i equal to 14 and 20 μM), for a plane sheet of thickness l, with uniform initial distribution and equal initial surface concentrations, can be estimated by using a solution of the Fick's second law equation,[36]

$$\frac{C_{\mathrm{ds,t}}}{C_{\mathrm{ds,eq}}} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2\pi^2\tau] \qquad (8)$$

where τ ($=Dt/l^2$) is the dimensionless time. For relatively small values of τ, sorption first-half time results ($C_{\mathrm{ds},t}/C_{\mathrm{ds,eq}} < 0.6$), eq. (8) reduces to

$$C_{\mathrm{ds,t}}/C_{\mathrm{ds,eq}} = (4/l).(tD/\pi)^{0.5} \qquad (9)$$

Diffusion coefficients of CR and CV can be calculated, giving values: D(CR, 14 μM) = 1.00 (±0.03) × 10^{-12} m^2 s^{-1}, D (CR, 20 μM) = 1.05 (±0.03) × 10^{-12} m^2 s^{-1}, D (CV, 7 μM) = 4.19 (±0.05) × 10^{-13} m^2 s^{-1}, and D (CV, 10 μM) = 5.27 (±0.04) × 10^{-13} m^2 s^{-1}.

The diffusion of CR is concentration independent and one order of magnitude higher than those found for CV. The analysis of diffusion coefficients of CV shows that: (a) they are of the same order of magnitude of those reported elsewhere for similar systems[37]; and (b) they are concentration dependent increasing by increasing the sorbed dye concentration. In a general approach, diffusion coefficients can be related to a frictional factor (which depends on the size of the diffusing molecules and viscosity) and an equilibrium thermodynamic factor for the change in chemical potential with concentration.[38] Therefore, the decrease in D with a diffusant concentration can be explained by a reduction in the thermodynamic factor (related to the variation of the activity coefficient with c), whereas the increase of D with concentration can be explained by a decrease of the resistance coefficient, which is a measure of the friction acting on a solute as it moves through a solvent.[39] Such a decrease in the resistance coefficient could be explained by the formation of solute–solute interactions and/or the decreasing of the effective water free volume. In the present case, we believe that the latter is the most probable reason for the increase of D with dye concentration.

CONCLUSIONS

Transport and sorption/desorption of CV, CR, and MTB through PVA membranes, obtained by a freezing/thawing technique, has been studied.

The diffusion of dyes through the PVA membrane was found to be dependent on the number and the type of ionic groups of the dye, or the dye type (anionic or cationic) and PVA–dye interactions. In the PVA/MTB system, the increase of the crystallinity degree is due to the interactions among the four carboxyl groups of the dye and the polymer through the hydrogen bonds. However, in the PVA/CR system, the interaction between CR and the PVA membrane leads to ionic complex formation. Both interactions hinder the permeation and lower the diffusion coefficient comparing with the CV diffusion coefficient. For the later dye, it has been found that the sorption of CV is accompanied by an increase of the CD, as observed by FTIR and DSC analysis. We can also conclude that the regeneration capacity of PVA decreases when the dye retention capacity increases.

In the dye concentration range studied, the sorption and desorption mechanism are essentially non-Fickian; however, it is worthwhile to note that as initial dye concentration increases the mechanism approaches to a pseudo-Fickian one.

All tested dyes diffuse through PVA membranes but not all of them permeate the PVA membrane plus that CV and CR are retained in a large percentage (58% for CV and 98% for CR) in the PVA membrane.

This formulation could be a starting material for the development of matrixes with very broad applications in terms of dye separation and purification.

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