

Effects of pH and Temperature on the Sorption of Sodium Dodecyl Sulfate by Cellulose Acetate/Polyaniline Blend Membranes

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ABSTRACT: Cellulose acetate/polyaniline (PANi) blends show a selective response to the presence of sodium dodecyl sulfate (SDS). Such detection can be monitored by visible absorption spectroscopy. In this article, we show how this is dependent on the pH and temperature. At pH 2, the redshift of the maximum absorbance wavelength of blend films is essentially dependent on hydrochloric acid; however, at pH 3, this effect clearly decreases, and at pH values between 4 and 6, the alteration of the blend color depends only on SDS. The selective detection of SDS is faster with a higher percentage of

PANi in the blend. At 25°C, the mechanism of sorption is essentially Fickian for short times, but this changes at higher temperatures, and at temperatures of 40°C and higher, the sorption kinetics show an initial time lag in which no visible response from the blend to SDS is detected. The response rate of blends to SDS detection increases with the temperature and PANi content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1947–1953, 2009

Key words: blends; colloids; conducting polymers; films; surfactants

INTRODUCTION

Polyaniline (PANi) is a remarkable polymer for various electroactive, optical, and anticorrosion applications, largely because of the presence of and possible interconversions between different oxidation states and protonated and deprotonated states.¹ Under most conditions, aniline polymers act as passive materials, but electrolysis or exposure to aqueous acidic solutions gives rise to conductive materials.^{2,3} The susceptibility of PANi to such protonation–deprotonation equilibria is important because it allows control of its conduction behavior, leading to changes of more than 2 orders of magnitude in the electrical conductivity.⁴

However, conductive polymers based on PANi possess poor physical and mechanical properties and are not soluble or processable in most common solvents. Numerous methods have been developed to overcome such shortcomings. There

are many known hybrid materials involving PANi and other polymer systems, such as pluronic polymers,⁵ polystyrene,⁶ and natural rubber,⁷ leading to blends with better mechanical and other properties.⁸

PANi-containing blends or composites,⁹ whose undiluted components have different properties, find applications in areas such as magnetic materials,¹⁰ corrosion protection,¹¹ and sensors.^{12,13}

Recently, we have shown that cellulose acetate (CA)/PANi blends have good mechanical properties¹⁴ and can be used for the selective detection of sodium dodecyl sulfate (SDS),^{15,16} the most important surfactant used in personal care and in industrial processes. In those studies, we showed that the sorption of SDS by PANi–CA is accompanied by a redshift in the maximum absorption wavelength in the visible spectrum. Although these blends have shown promising properties for sensing applications (e.g., they show an SDS detection limit less than 0.5 mM), they still present some drawbacks, such as slow response times. In this work, we investigate the effects of acidic pHs and temperature on the transport of SDS through CA–PANi blends. The effect of the PANi concentration in the blend is also considered. It is hoped that these results on SDS diffusion in CA–PANi blends will help in the design of systems with a faster response to the detection of SDS.

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EXPERIMENTAL

Reagents and polymeric films

High-purity PANi powder in its emeraldine base form was a gift from A. P. Monkman (Durham University, Durham, United Kingdom) and was prepared by chemical polymerization.¹⁷ CA was purchased from Aldrich (Steinheim, Germany) and had a weight-average molecular weight of 30,000 with 39.8 wt % acetylation. Solutions of SDS (10 mM; Aldrich) were prepared with Millipore Milli-Q water. Tetrahydrofuran (THF; Riedel-de H en, Seelze, Germany) and methanoic acid (formic acid; Aldrich) were used as received. The polymeric films were obtained by the dissolution of CA in THF and PANi in HCOOH. After approximately 30 min of continuous stirring of the individual solutions, they were mixed and left stirring for another 24 h. The solution, which had a clear homogeneous aspect, was then deposited as a film on a flat glass support with a Simex automatic film applicator. After complete evaporation of the solvent at room temperature, the membrane was removed from the glass support with the help of water and dried with an infrared lamp. The thickness of the polymeric membranes was measured with a Mitutoyo digimatic micrometer (± 0.001 mm). Four blend films and a blank were prepared with the following compositions: M0, 15% (w/v) CA; M1, 15% (w/v) CA and 0.025% (w/v) PANi; M2, 15% (w/v) CA and 0.050% (w/v) PANi; M3, 15% CA (w/v) and 0.075% PANi (w/v); and M4, 15% CA (w/v) and 0.10% PANi (w/v). All membranes deposited from a 3 : 1 THF/HCOOH mixture were macroscopically homogeneous and showed a blue transparent aspect.

Ultraviolet-visible spectroscopy

Ultraviolet spectra were obtained with a Jasco (Essex, UK) V-530 spectrophotometer; the spectra of films inserted directly into the cell compartment were obtained and studied over the wavelength range of 400–800 nm with a bandwidth of 1.0 nm. The effect of the solution (HCl and SDS–HCl at different concentrations) on each blend film was measured as follows: each blend sample remained in the appropriate solution (HCl, SDS, or SDS/HCl) during the stated time, the film was then removed, and after off any drops of the solution were wiped off, the spectrum was taken at a given recorded time.

pH measurements

The kinetics of sorption of SDS by the membranes were studied at various pH values between 2 and 6. The pH was controlled by the addition of hydrochloric acid to the SDS solutions to produce a concentra-

tion in the range of 10^{-2} to 10^{-5} M. pH measurements were carried out with a Radiometer (Lyon, France) PHM 240 pH meter with an Ingold U457-K7 pH conjugated electrode; the pH was measured in fresh solutions, and the electrode was calibrated immediately before each experimental set of solutions with pH 2, 4, and 7 buffers recommended by the International Union of Pure and Applied Chemistry. From pH meter calibration, a zero pH of 6.65 (± 0.04) and a sensitivity of 99.1% were obtained.

Experiments on the diffusion of 10 mM HCl through polymer blends were carried out in the following way: a blend sample was introduced into a cell similar to that described elsewhere,¹⁸ and an HCl solution was placed in contact with one surface of the blend. The HCl flux through the membrane was monitored with a combined pH electrode through the recording of the increase in the pH as a function of time.

RESULTS AND DISCUSSION

Sorption of HCl by PANi–CA blend films

The spectroscopic properties of PANi depend on the intrinsic redox states of PANi, which depend on the protonation degree.^{19,20} Therefore, the transport by diffusion of an acid, such as hydrochloric acid, will provide important information about the protonation mechanism (e.g., see ref. 21 for PANi in CA–PANi blend membranes).

Sorption kinetics of the sorbed species can be quantified with Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where D is the diffusion coefficient, C is the concentration of the sorbed species, x is the space coordinate, and t is the time. For a plane sheet of thickness l , with a uniform initial distribution and equal initial surface concentrations, Fick's second law leads to the following analytical equation:²²

$$\frac{C_t}{C_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-(2n+1)^2 \pi^2 \tau] \quad (2)$$

where C_t and C_∞ are the concentrations of sorbed species at time t and at infinite time, respectively, and $\tau = Dt/l^2$ is the dimensionless time.

For relatively small values of τ [the sorption first half-time results ($C_t/C_\infty < 0.6$)], eq. (2) can be reduced to

$$C_t/C_\infty = (4/l)^* (tD/\pi)^{0.5} \quad (3)$$

Figure 1 shows the sorption kinetics of HCl by CA and CA–PANi blend films.

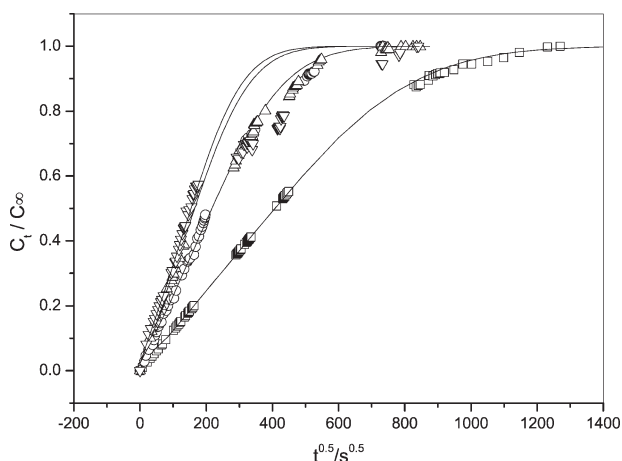


Figure 1 Sorption kinetics of 0.1 mM HCl by CA-PANi blend films: (\square) M0 (I), (\circ) M2 (II), (\triangle) M3 (III), and (∇) M4 (IV). The solid lines (I-IV) represent C_t/C_∞ predicted by eq. (2), taking into account D as described in the text.

HCl sorption by all polymeric matrices shows a linear dependence on the square root of time as predicted by eq. (3) for $C_t/C_\infty < 0.6$. Under these conditions, the diffusion coefficient of HCl (D_{HCl}) can be calculated: $D_{\text{HCl}}(\text{M0}) = 4.88 (\pm 0.02) \times 10^{-12} \text{ cm}^2/\text{s}$, $D_{\text{HCl}}(\text{M2}) = 1.68 (\pm 0.04) \times 10^{-11} \text{ cm}^2/\text{s}$, $D_{\text{HCl}}(\text{M3}) = 2.82 (\pm 0.02) \times 10^{-11} \text{ cm}^2/\text{s}$, and $D_{\text{HCl}}(\text{M4}) = 3.53 (\pm 0.12) \times 10^{-11} \text{ cm}^2/\text{s}$. These D_{HCl} values, obtained by a non-steady-state method, are of the same order of magnitude as those found in CA derivatives with a steady-state method²³ but are much lower than those found by the transport of HCl in PANi membranes;²⁴ this shows that CA and CA-PANi blend films have high resistance to HCl transport.

It is interesting to note that there is a linear relationship between D_{HCl} and the amount of PANi in the blends. This is a direct result of the structural alterations produced by PANi in the blends. PANi induces a lamellar structure into CA, increasing the free volume available for diffusion.¹⁴ Another factor that is likely to be affected by an increase in the PANi content in blends is the deviation of the sorption of the acid from the Fickian mechanism (for $C_t/C_\infty > 0.6$). This can be explained by the interaction with aniline groups: the diffusion will be followed by specific interactions between imine nitrogens and H^+ ions, with a consequent alteration in the oxidation state of PANi from emeraldine to leucoemeraldine. This protonation process can easily be followed by visible spectroscopy (see the next section for a detailed discussion).

Effect of pH and SDS on the chromic response of PANi-CA films

The chromic properties of PANi and PANi-CA blend films are strictly dependent on the oxidation state of PANi; the preparation of PANi-CA blend films with PANi in its emeraldine base form produces transparent green films^{14,19} with a maximum absorbance wavelength of 580 nm. In the presence of SDS, a displacement of the maximum absorbance wavelength to around 770 nm occurs (Fig. 2). This phenomenon has been discussed on the basis of the change in the overall PANi planarity. The incorporation of very small amounts of PANi into CA is enough to obtain a lamellar membrane,¹⁴ and so CA-PANi blends reproduce Helfrich membranes.^{25,26} However, it is known that

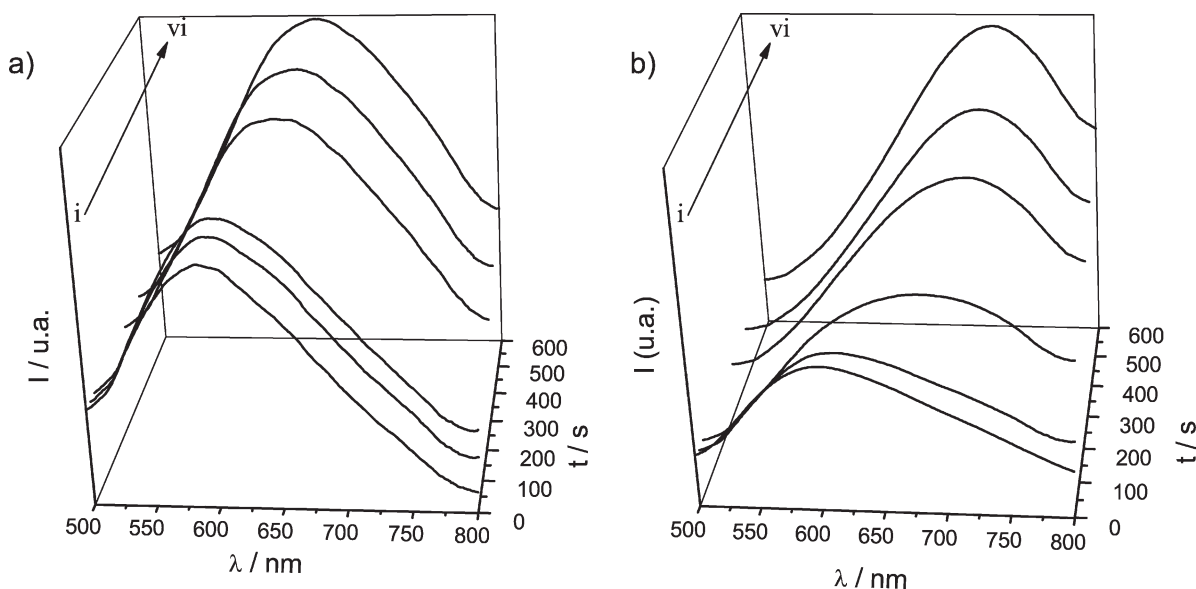


Figure 2 Effects of (a) 1 mM HCl sorption and sorption time on the visible spectra of M2 at 25°C and (b) 1 mM HCl and 10 mM SDS sorption and sorption time on the visible spectra of M2 at 25°C: (i) 0, (ii) 30, (iii) 60, (iv) 300, (v) 420, and (vi) 600 s.

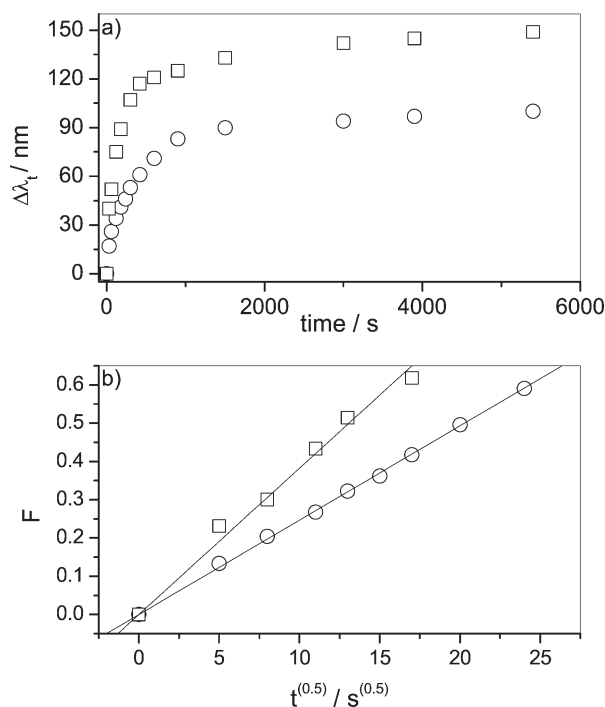


Figure 3 (a) Experimental and (b) short-time-range-normalized sorption kinetics of (○) 10 mM HCl and (□) 10 mM HCl/SDS at pH 3 by M3 at 25°C, as shown by $\Delta\lambda_t$. The solid lines in part b were calculated by the fitting of the experimental data to eq. (4).

similar effects on the visible spectra of PANi can be found when the protonation of imine groups takes place by contact with HCl.⁴ In this section, the effect of an acidic medium on the detection of SDS by CA-PANi blend films, on the basis of visible spectroscopy, is analyzed and discussed with the effect of the presence of HCl.

Figure 3(a) shows the shift in the maximum absorbance wavelength ($\Delta\lambda_t$) of M3 (see the Reagents and Polymeric Films section) in aqueous solutions of SDS/HCl (10 mM/pH 3) and HCl (pH 3).

There is a rapid alteration of $\Delta\lambda_t$ within the first few minutes of sorption (ca. 15 min), and this is followed by a slower approach to equilibrium. The maximum absorbance wavelength at equilibrium ($\Delta\lambda_{eq}$) was measured after 24 h, and in this case, the measured values were 173 and 123 nm, respectively.

If we assume that $\Delta\lambda_{eq}$ is proportional to the concentration of sorbed molecules,¹⁵ the sorption kinetics can be evaluated with the following empirical equation:²⁷

$$F = \Delta\lambda_t / \Delta\lambda_{eq} = kt^n \quad (4)$$

where f is a flux, k is a kinetic constant related to D [see eq. (3)], and n is the diffusional exponent, which suggests the nature of the sorption mechanism. A value of $n = 0.5$ indicates Fickian case I transport (mechanism), whereas $n = 1$ is used for case II trans-

port. In case II diffusion, the solute diffusion rate is faster than the polymer relaxation rate, whereas in case I, the solute diffusion rate is slower than the polymer relaxation. The intermediate values, ranging from 0.5 to 1.0, are indicative of anomalous transport, which is characterized by the solvent diffusion rate and the polymer relaxation being about the same order of magnitude.^{22,28–30} In this case, eq. (4) with $n = 0.5$ fits experimental data for $F < 0.6$,^{31,32} and this shows that the kinetics, for short times, follow Fickian behavior. Representative sorption uptake as a function of the half-time ($t^{0.5}$) is shown in Figure 3(b).

Taking into account the discussion of the HCl kinetics in the previous section and data reported elsewhere²³ for similar systems, we can conclude that the wavelength displacement is due to a fraction of the total amount of sorbed particles (HCl, SDS, or both); that is, the concentration of sorbed molecules has two contributions, those due to the immobilized molecules and those due to the free molecules. Because in all the analyzed systems the alteration in the color of the blend film can be explained by Fickian behavior, it seems reasonable to conclude that the main parameter controlling the chromic response of PANi-based blend films is the concentration of uncomplexed sorbed species.

The study of color change kinetics is of great practical importance, both because the experimental detection of SDS by these blends must be fast for practical applications and because it can give us information about the mechanisms involved. Figure 4 shows the k values for the sorption of aqueous SDS/HCl and HCl solutions by films of CA-PANi blends. From the data shown in Figure 4, the following further general observations can be made: (1) the k values for HCl sorption decrease with the concentration

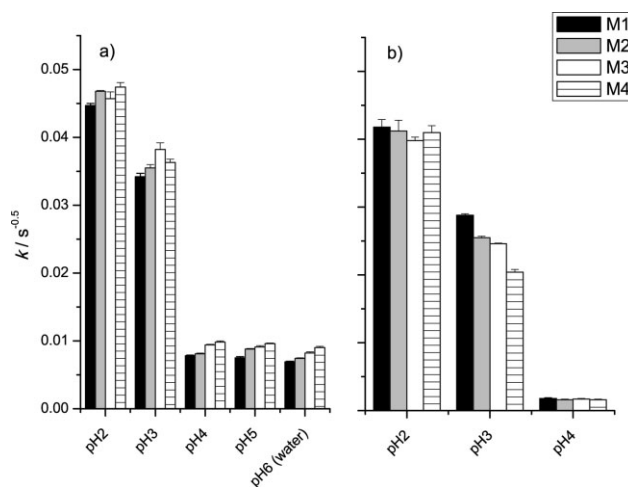


Figure 4 k values [eq. (3)] for the sorption of (a) SDS/HCl and (b) HCl by different PANi-CA blend films, as shown by visible spectroscopy.

gradient decreasing, no alteration in the blend color can be noted within the first hour of the experiment for HCl at pH 5, and residual alterations can be noted at pH 4; (2) a similar trend can be observed for SDS/HCl sorption, but even in the absence of HCl, the blend can detect the presence of SDS; and (3) the kinetics of SDS detection do not change for pHs greater than 3.

Further discussion can be made on the basis of the data shown in Figure 3. It is worth noting that, with a few exceptions, the flux increases as the content of PANi increases in the polymer blend. This is in good agreement with the fact that in the presence of increasing amounts of PANi, the free volume of the polymeric matrix also increases (see the following discussion).

The redshifts observed in the blend film at different pH values are markedly dependent on SDS; at pH 2, the response to SDS sorption, as shown by the color change, is notably faster than that observed for HCl sorption. In contrast, at pH 6, no redshift can be observed when the film is immersed in an aqueous HCl solution, but a marked wavelength displacement can be observed in the presence of SDS. Similar behavior has been found for other polymer blends. In fact, in all of them, we could observe a color change from blue to green when they were immersed in SDS solutions. This clearly suggests that such a color change depends not only on the protonation of imide groups but also on possible hydrophobic interactions.¹⁵

It is also of interest to compare the sorption kinetics of 0.1 mM HCl as shown by visible spectroscopy and by potentiometry. Taking k values shown in Figure 4(b) for a film thickness of 8 μm , we find that D_{HCl} is equal to $1.13 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for films M1 and M4 and $1.00 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for films M2 and M3, as calculated by eq. (3). These values are of the same order of magnitude as those reported in the previous section. Although the absolute values are slightly smaller, considering the experimental error, we can conclude that the agreement is quite good, and this once more shows that the alteration of color of PANi-CA films is dependent on the total sorbed concentration of HCl.

The next challenge is to try to evaluate what the contribution of SDS is to this change; it is known that the displacement of the maximum absorbance wavelength ($\Delta\lambda$) is dependent on both SDS and pH (within the range of 2–4); because the pH can affect only the micelle properties of SDS,³³ it is reasonable to consider that $\Delta\lambda$ of blends can be described as a sum of two different independent contributions:

$$\Delta\lambda = \Delta\lambda_{\text{HCl}} + \Delta\lambda_{\text{SDS}} \quad (5)$$

where $\Delta\lambda_{\text{HCl}}$ and $\Delta\lambda_{\text{SDS}}$ are the displacements of the maximum absorbance wavelength due to HCl and

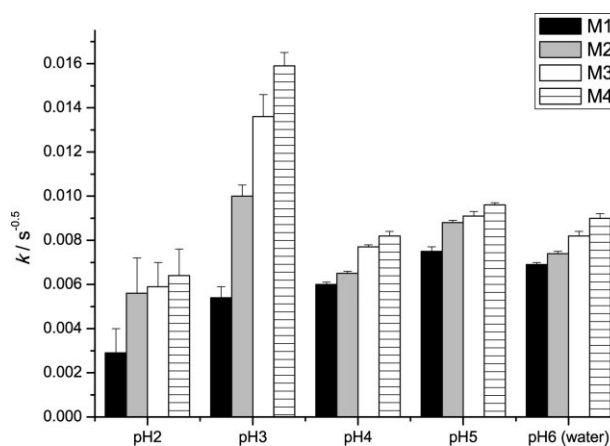


Figure 5 Contribution of SDS to the kinetics of SDS detection by different PANi-CA blend films at different pH values at 25°C.

SDS, respectively. Consequently, on the basis of the data shown in Figure 4, it is possible to calculate k for SDS sorption by PANi-CA films (Fig. 5). At all pH values, the flux of SDS increases with the content of PANi increasing, and this can be explained by an increase in free volume induced by the lamellar structure of PANi.

At higher pH values (4–6), SDS detection does not significantly change with the pH, and this can be readily explained by the fact that only SDS contributes to the alteration in the color change of the polymeric blend films.

It is interesting to note that the fastest response to SDS detection is obtained at pH 3; comparing the data shown in Figures 3 and 4, we can observe that at pH 2, the spectroscopic response from the blends is clearly controlled by HCl; however, at pH 3, with an increase in the PANi content in the blends, the chromic response becomes much more sensitive to the presence of SDS. Although we do not yet have an explanation for this, we believe that it is due to the balance between two competing processes resulting from the protonation of PANi. Further work is in progress to try to clarify this.

Effect of temperature on the kinetic chromic response of PANi-CA films to SDS

To check how the temperature affects the chromic response of PANi-CA films to the presence of SDS, experiments on the sorption kinetics of 10 mM SDS by M2 and M4 films at different temperatures (from 25 to 70°C) were carried out.

Figure 6 shows the kinetics of 10 mM SDS transport through film M2 at different temperatures. The sorption mechanism seems to be rather complex. At 25°C, the results are in reasonable agreement with those reported in the previous section; at $F < 0.6$, k [eq. (3)] is equal to $0.0077 (\pm 0.0001)$ and 0.0074

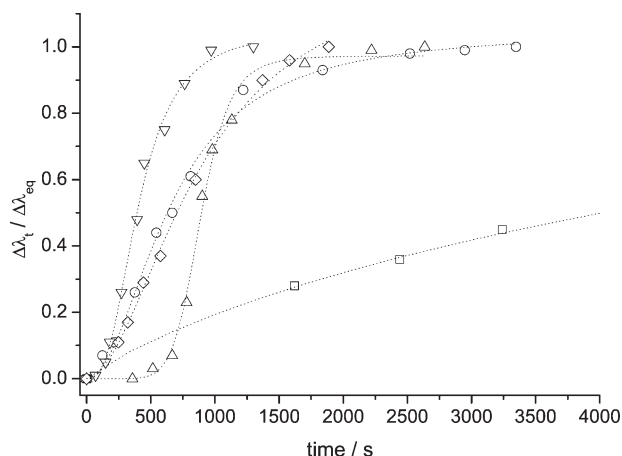


Figure 6 Kinetics of color changes of M2 films in the presence of SDS at different temperatures: (□) 25, (○) 40, (△) 50, (▽) 60, and (◇) 70°C. Dashed lines are just guides.

(± 0.0001) $s^{-1/2}$. When the temperature increases, we can observe a time delay before any measurable response of the polymer blend to SDS detection is observed. However, when such a time lag is reached, a rapid increase in F with time occurs (until values ca. 0.6), and it is faster at higher temperatures. We now need to quantify such variables; a simple approach is to consider the velocity of the polymeric blend color change (v) as dependent on the concentration of the sorbed species as measured by $\Delta\lambda$:

$$v = dF/d(t - \theta)^2 \quad (6)$$

where θ is the time lag.

Table I shows the parameters (v and θ) that best fit the experimental results of the sorption kinetics to eq. (6); Origin 7.5 software was used with a confidence interval of 95%. From the fitting parameters given in Table I, we can conclude that the time lag and v increase with the temperature increasing. It is known that soft membranes exhibit thermal fluctuations, and the out-of-plane incoherent undulation fluctuations in a stacked-membrane system are sup-

pressed by the spatial confinement due to neighboring polymer chains in the membranes.³⁴ Losing entropy induces intermembrane repulsive interactions that stabilize the smectic order. Because of the intrinsically long-range nature of these interactions, the lamellar spacing of a Helfrich system can be easily expanded up to the wavelength of visible light.^{25,26} The smectic order of a Helfrich system is stabilized by out-of-plane incoherent undulation fluctuations of membranes, and this means that manipulation of such fluctuations directly affects the degree of the smectic order. Recently, it has been demonstrated that the insertion and manipulation of motion of electrically driven colloidal particles allow the control of the degree of the smectic order.³⁵ It has also been found that by the doping of membranes with a surfactant, even without the application of any electrical field, the Bragg peak is displaced to the red by the alteration of the smectic order of the polymer. The incorporation of very small amounts of PANi into CA is enough to obtain a lamellar membrane,¹⁴ and so PANi-CA blends reproduce Helfrich membranes. It should also be expected that, with the temperature increasing, the free volume present in these soft membranes will increase, and consequently, the time necessary to start observing a red displacement of the blends will increase. The rate of color change increases with the temperature increasing and, to some extent, with the PANi content increasing; this is also in agreement with the previous justification because increasing the PANi content increases the probability of the formation of a Helfrich-type system and increasing the temperature also increases the interactions affecting such a system.

A further important point is that on the basis of the rate of the blend response to the presence of SDS by a change in its color, the activation energy (E_D) can be calculated with the Arrhenius relationship:

$$v = A \exp(-E_D/RT) \quad (7)$$

where A is the pre-exponential factor, R is the gas constant, and T is the temperature. The values of E_D ,

TABLE I
Fitting Parameters of the Sorption Kinetics of SDS in M2 and M4 PANi-CA Blends at Different Temperatures According to Eq. (6) at $F < 0.60$

Temperature (°C)	M2		M4	
	v ($10^{-3} s^{-1}$)	θ (s)	v ($10^{-3} s^{-1}$)	θ (s)
25	—	0	—	0
40	0.75 (0.03)	24 (3)	0.71 (0.02)	84 (21)
50	0.80 (0.03)	104 (17)	0.79 (0.07)	354 (97)
60	1.62 (0.15)	127 (19)	2.98 (0.05)	403 (12)
70	2.33 (0.22)	676 (78)	3.10 (0.10)	610 (33)
E_D (kJ/mol)	6.4 (0.3)		6.1 (0.2)	

Values inside parentheses are standard deviations.

shown in Table I, show that the chromic response is not diffusion-controlled; the values of E_D are almost the same for blends with different amounts of PANi.

CONCLUSIONS

The detection of SDS by PANi-CA, as shown by visible absorption spectroscopy, is independent of the pH for pH values greater than 3. At lower pH values, the redshift of the CA-PANi films is also affected by the presence of HCl. The kinetics of SDS sorption normally increase in blends with higher concentrations of PANi. We have also found that the sorption kinetics can be modeled by Fickian behavior for short-range times ($F < 0.6$). These results clearly suggest that the sorption of SDS is the main factor affecting the color change of PANi-CA blend films. At low pH values (2 and 3), the protonation of PANi imide groups occurs, and the electrostatic interaction between SDS and PANi must be the most important interaction affecting the global chromatic response of the blend.

This is in close agreement with our previous hypothesis that the detection of SDS by PANi-CA can be explained by changes in the smectic order of the polymer.

The effect of temperature also provide information about the importance of the structure of PANi in the blend. With an increase in the temperature, thermal fluctuations of soft membranes cannot be neglected, and consequently, the SDS sorption mechanism is no longer Fickian. It has been found that with the temperature increasing (from 40 to 70°C), there is a time lag for the detection of SDS. This time lag increases with the temperature. However, after such a time lag, the detection limit is quite dependent on the temperature and PANi concentration.

These data will contribute to the development of PANi sensor blends with the fastest optical response to and lowest detection limit for the presence of SDS.

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