Adsorption of Nile Red by Poly(*N*-isopropylacrylamide) Gels in Binary Water/Tetrahydrofuran Mixtures

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ABSTRACT: The adsorption of Nile Red by poly(*N*-isopropylacrylamide) (PNIPAM) gels in binary water/tetrahydrofuran solutions was investigated using absorption spectrophotometry as a function of the volume fraction of THF, φ. Due to the cononsolvency abilities of such binary solvent mixtures, deswelling of the PNIPAM gels is observed in water-rich mixtures, $0 \leq \varphi \leq 0.6$, while the gels reswell for $\varphi > 0.6$. The position of the absorption band of Nile Red before and after equilibration with the PNIPAM gels indicates that the composition of the external solvent mixture is not practically influenced by the swelling process.

On the other hand, it is found that the gels can effectively adsorb Nile Red in water-rich mixtures ($\varphi < 0.6$), whereas no significant adsorption was observed in tetrahydrofuran-rich mixtures. In fact, about 80% of the dye is adsorbed by the PNIPAM gels, at $\varphi = 0.2$. Under these conditions, the rather shrunk PNIPAM gel offers a more convenient less polar environment for Nile Red than the water-rich bulk solvent. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1509–1514, 2010

Key words: poly(*N*-isopropylacrylamide); hydrogel; cononsolvency; adsorption; dye

INTRODUCTION

Hydrogels are three-dimensional chemically cross-linked polymer networks, able to swell in water or other polar solvents, increasing substantially their original volume while keeping their integrity. Among other applications, hydrogels are widely studied for possible environmental applications, especially as it concerns the waste water treatment.[1–9] In fact, it is known that charged hydrogels are able to adsorb effectively from water oppositely charged organic pollutants. Thus, numerous studies have been devoted to the adsorption of cationic dyes, used as model pollutants, by anionic hydrogels[10–17] containing weakly acidic or strongly charged groups. In contrast, the use of nonionic hydrogels for the adsorption of organic dyes is much less reported, as the polymer-organic solute interactions are much weaker. In these cases, other driving forces for the effective adsorption of the organic dyes can be exploited, for instance hydrogen-bonding or hydrophobic interactions.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a widely known thermosensitive nonionic water-soluble polymer, exhibiting a lower critical solution temperature (LCST) behavior in aqueous solution at $\sim 32°$C.[18–20] Thus, while being hydrophilic and water-soluble at ambient temperature, it turns to hydrophobic and water-insoluble as temperature increases above LCST. Respectively, for chemically cross-linked PNIPAM chains, the initially swollen hydrogel collapses upon warming above $\sim 32°$C. Based on this property, numerous "smart" applications have been proposed, mainly for the entrapment and temperature-controlled release of hydrophobic drugs.[20,21] Within the frame of such applications, the investigation of the adsorption of hydrophobic dyes by *N*-isopropylacrylamide-containing hydrogels or membranes, eventually as a function of temperature, is of interest.[22,23]

Related to the LCST behavior, another interesting property of PNIPAM is the so-called cononsolvency behavior exhibited by this polymer in binary mixtures of water with several polar organic solvents, such as methanol, tetrahydrofuran and dioxane.[24–29] As known, cononsolvency describes the situation of polymers soluble in two pure solvents but insoluble in the binary solvent mixtures, for some mixture compositions. In fact, PNIPAM chains present an LCST-type cononsolvency behavior in some water-rich binary solvent mixtures, while PNIPAM gels[30–38] collapse under similar mixing conditions.

In the present study we investigate whether the ability of PNIPAM hydrogels to adsorb hydrophobic dyes may be observed under cononsolvency conditions. Tetrahydrofuran (THF) was chosen as the polar solvent forming cononsolvent mixtures with water for PNIPAM. Moreover, Nile Red (Fig. 1) was
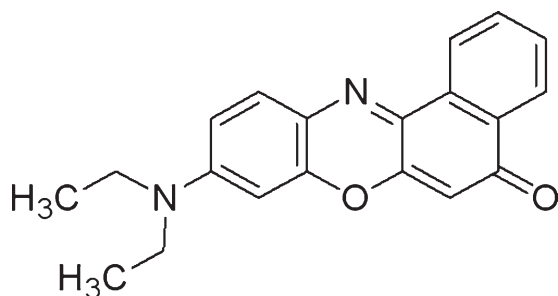
Figure 1 Structural formula of Nile Red.

chosen as a model dye, as it is known that its optical properties (absorption and emission) are strongly dependent on the polarity of the environment. In fact, the absorption band of Nile Red in the visible region shifts to lower wavelengths while the emission of the dye is greatly quenched as the water-content of binary water/organic solvent mixtures increases. Because of these properties, Nile Red has been widely used in biology to stain intracellular lipids or phospholipid bilayer membranes,[39] as well as in the investigation of disperse systems like microemulsions[40,41] and micelles.[42]

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAM), methylene bisacrylamide (BIS), sodium metabisulphite ($Na_2S_2O_5$), ammonium persulphate (($NH_4)_2S_2O_8$), *N,N,N′,N′*-tetramethylethylene diamine (TEMED), and HPLC-grade tetrahydrofuran were purchased from Aldrich. Nile Red ($C_{20}H_{18}N_2O_2$, purity 99%) was purchased from Acros Organics. Water was purified by means of a Seralpur Pro 90C apparatus combined with a USF Elga laboratory unit.

The homopolymer PNIPAM was prepared by free radical polymerization in water at 29°C, using the redox couple ammonium persulphate/sodium metabisulphite as initiator.[43]

The PNIPAM gel was prepared by dissolving NIPAM (1 *M*) and BIS (2 mol % over the NIPAM concentration) in water under stirring at room temperature. The solution was deoxygenated and then ammonium persulphate and TEMED were added. The formation of the gel was almost immediate. The reaction was let to proceed for some hours and then the gel was immersed in pure water for one week. Water was renewed daily. Finally, the hydrogel was cut in small pieces and freeze-dried.

Reduced viscosity study

The reduced viscosity study was carried out at 25°C with an automated viscosity measuring system

(Schott-Gerate AVS 300) equipped with a micro-Ostwald-type viscometer. The polymer concentration was fixed at 2.5×10^{-3} g/cm^3.

Swelling experiments

For the swelling measurements, a preweighted dry gel sample was immersed in 10 cm^3 of the solvent with the desired mixture composition and let to swell. The mass of the gel was measured daily. The gel was considered to reach equilibrium when its mass did not change (within experimental error) for at least two days. For each experimental point, at least two samples were measured. The deviation of the results was less than 5%.

Adsorption study

The appropriate volume of a methanolic stock solution of Nile Red (10^{-3} *M*) was added to the desired solvent mixture (10 cm^3). Then, a 0.05 g piece of the PNIPAM gel was immersed in each solution and was let to equilibrate at 25°C for 2 days. The absorption spectrum of the solution, before and after equilibration with the PNIPAM gel was monitored using a Hitachi spectrophotometer, model U 1800.

RESULTS AND DISCUSSION

Cononsolvency in binary water/THF mixtures

The viscometry behavior of linear PNIPAM chains is compared in Figure 2 with the swelling behavior of PNIPAM gels in binary water/THF mixtures. The results, are plotted as a function of the volume fraction φ of THF in the binary mixture,

$$\varphi = V_{THF}/(V_{THF} + V_{water}) \qquad (1)$$

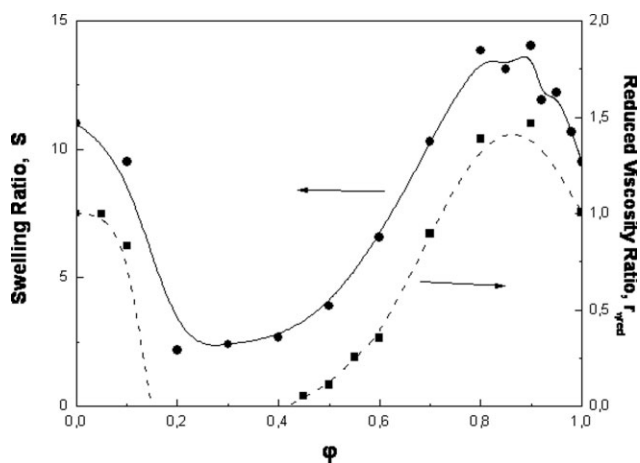**Figure 2** Variation of the swelling ratio, S of the PNIPAM gels (●), or the reduced viscosity ratio, $r_{\eta red}$, of the linear PNIPAM homopolymer (■) with the volume fraction of THF, φ, in binary water/THF solvent mixtures.

where V_{THF} and V_{water} are the volumes of THF and water, respectively.

For the viscometry results, the reduced viscosity ratio $r_{\eta red}$ is used, defined as

$$r_{\eta red} = \eta_{red}/(\eta_{red})_{water} \qquad (2)$$

where η_{red} and $(\eta_{red})_{water}$ are the reduced viscosities of the linear PNIPAM chains in the actual solvent mixture and in water, respectively. Thus, $r_{\eta red}$ values lower or higher than unity indicate a shrinkage or an expansion of the PNIPAM chains, respectively, in comparison with their hydrodynamic volume in pure water. As seen, the value of $r_{\eta red}$ in pure THF is also close to unity, suggesting that the hydrodynamic volume of the polymer chains is similar in both pure solvents. Upon addition of THF in water, $r_{\eta red}$ decreases significantly, indicating that the polymer chains shrunk, as the binary mixture tends to a cononsolvent. In fact, for $0.15 < \varphi < 0.4$, the solutions turn turbid and macroscopic phase separation is observed. Further addition of THF improves the quality of the solvent mixture and the solutions become homogeneous, while $r_{\eta red}$ increases gradually, suggesting that the polymer chains start to "sense" a good solvent. Interestingly, a slight maximum is observed at $\varphi = 0.8$–0.9, possibly indicating that these binary solvent mixtures are better solvents for PNIPAM, as compared to pure water or pure THF. It should be noted that a qualitatively similar behavior has been also observed for PNIPAM in water/dioxane mixtures.[36]

The conformational changes of linear PNIPAM chains in binary water/THF mixtures can be followed macroscopically by the respective variation of the swelling ratio, S, of the PNIPAM gels in these binary mixtures. S is defined as

$$S = w_s/w_d \qquad (3)$$

where w_d and w_s is the mass of the gel before (dry) and after (swollen) equilibration with the solvent mixture, respectively. As seen, the initially swollen PNIPAM hydrogel (S ∼ 11) collapses upon addition of THF, so that a swelling ratio of just ∼ 2 is found at the region $\varphi = 02$–0.4, where phase separation of the linear PNIPAM chains was observed. In accordance with the variation of $r_{\eta red}$, as φ increases further the PNIPAM gels reswell gradually to reach a swelling ratio S ∼ 8 in pure THF, after passing through a maximum at $\varphi = 0.8$–0.9.

Adsorption study

The possible adsorption of Nile Red by the PNIPAM gels in binary water/THF mixtures was studied exploiting the absorption band in the visible region of the UV-vis spectrum of the dye. Some representa-
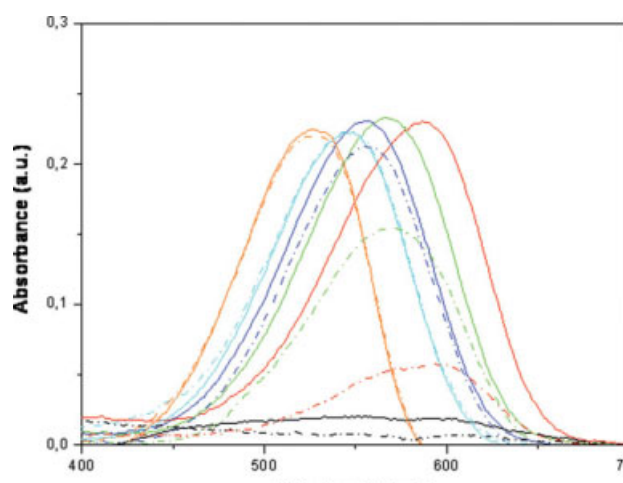
Figure 3 Absorption spectra of Nile Red in binary water/THF mixtures, before (solid lines) and after (dotted lines) equilibration with PNIPAM gels. The volume fraction of THF, φ, is 0 (——), 0.2 (——), 0.4 (——), 0.6 (——), 0.8 (——), and 1 (——). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

tive spectra of Nile Red in such binary mixtures, before (full lines) and after (dotted lines) equilibration with the PNIPAM gels, are shown in Figure 3. While Nile Red is readily soluble in organic solvents, its solubility in water is very poor (<1 μg/mL).[44] As seen, due to the solubility problems of the dye in water under our experimental conditions (the concentration of the dye is ∼ 2 μg/mL), the absorption band of Nile Red in pure water is hardly detectable. Probably, the same problem holds partly in the solvent mixture with $\varphi = 0.1$, where a relatively weak absorption peak is detected. Nevertheless, for THF-richer solvent mixtures, the absorption band of Nile Red is clearly observable. The shift of this band towards lower wavelength with increasing the THF content reflects the well-known sensitivity of this probe to the polarity of the solvent. Similar trends are also observed after equilibration of these solutions with the PNIPAM gels. The most important difference is the lower intensity of the absorption bands for the water-rich mixtures. This behavior suggests that in the water-rich region which practically coincides with the cononsolvency region discussed in Figure 2, the PNIPAM gels do adsorb the dye and the Nile Red concentration in the external solution decreases substantially. However, the adsorption ability of the PNIPAM gels weakens upon increasing the THF content, so that the absorption bands of Nile Red before and after equilibration with the PNIPAM gels become identical in pure THF or in THF-rich mixtures.

To better quantify these observations, in Figure 4 we present the variation of the absorption of Nile
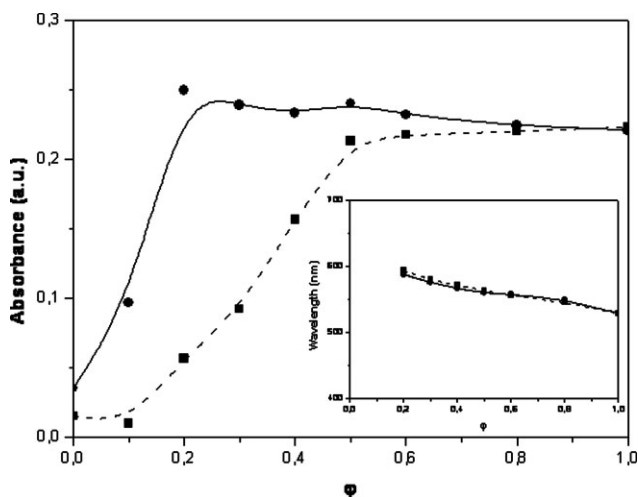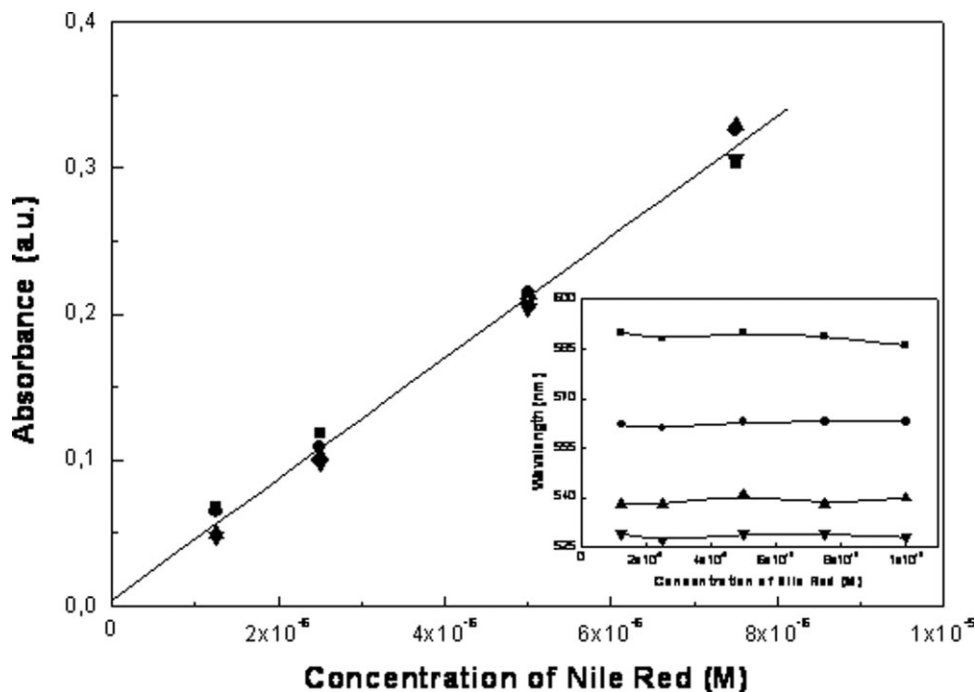
Figure 4 Dependence of the maximum absorbance and the position of the peak (inset) of Nile Red on the volume fraction of THF, φ, in binary water/THF mixtures before (●) and after (■) equilibration with PNIPAM gels.

Red at each peak with the volume fraction of THF, φ, before and after equilibration with the PNIPAM gels. Before the immersion of the gels, the intensity of the absorption of Nile Red starts from a low value in pure water and increases abruptly upon addition of THF up to φ = 0.2, where the curve seems to reach a "plateau." This suggests that for φ ≥ 0.2, the extinction coefficient of Nile Red is not significantly dependent on the composition of the solvent mixture. After equilibration with the PNIPAM gels, the

absorption intensity of Nile Red in the external solution is practically zero for φ = 0 and φ = 0.1 and it gradually increases with increasing the THF content up to φ = 0.5–0.6. As a consequence, while the intensity difference before and after equilibration with the PNIPAM gels is very important at φ = 0.2, this deviation gradually weakens up to φ = 0.5–0.6 and it becomes negligible (within the experimental error) for higher THF contents.

The position of the absorption band of Nile Red in the water/THF mixtures, before and after equilibration with the PNIPAM gels, is presented in the inset of Figure 4 as a function of φ. It is seen that the two curves practically coincide (at least for φ > 0.2, where the absorption band of Nile Red is clearly detectable for both series of experiments. This suggests that, under the experimental conditions applied here, the actual composition of the external solvent remains practically identical to the initial composition, at least as it is "sensed" by Nile Red. Consequently, the intensity variations shown in Figure 3 can be attributed to the respective variations of the adsorption of Nile Red by the PNIPAM gels and not to solvent composition variations.

To determine the variation of the adsorption of the dye by the PNIPAM gels with the solvent composition, we have constructed the calibration curves for several solvent compositions (at the corresponding wavelength of the peak, each time), covering the range 0.2 ≤ φ ≤ 1. The results are shown in Figure 5, while in the inset in the same figure the position of

Figure 5 Variation of the maximum absorbance and the position of the peak (inset) with the concentration of Nile Red in binary water/THF mixtures. The volume fraction of THF, φ, is 0.2 (■), 0.5 (●), 0.8 (▲), and 1 (▼).
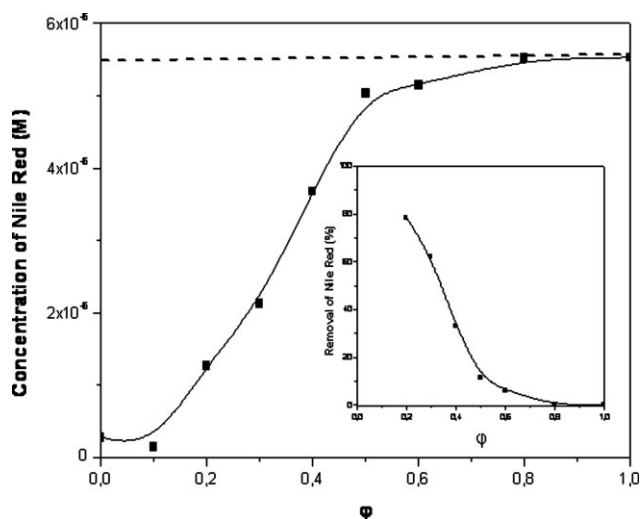
Figure 6 Dependence of the concentration of Nile Red in the external solutions with the volume fraction, φ, of binary water/THF solvents, after equilibration with the PNIPAM gels. The dashed line indicates the initial concentration of Nile Red in the binary solvent mixtures. Inset: Variation of the % removal of Nile Red from the binary water/THF mixtures.

the respective peaks is presented as a function of the Nile Red concentration for the binary solvent mixtures studied. As seen, the position of the peaks is essentially independent on the concentration of Nile Red for each solvent mixture, within the concentration range studied. Moreover, while there are slight differences with the solvent composition, at a first approximation we can consider that, within this φ region, the Beer-Lambert Law is obeyed and it does not depend significantly on φ, as all results seem to follow the same linear master.

From the thus determined Beer-Lambert's law and the results shown in Figure 4, the concentration of Nile Red in the external solutions after equilibration with the PNIPAM gels can be estimated (Fig. 6). The concentration of the dye in all these solvent mixtures before the immersion of the PNIPAM gels, represented by the dashed line, was similarly estimated from the absorption of the initial solutions and it was found 5.5×10^{-5} M. After equilibration, the concentration of Nile Red in the external solution starts from substantially lower values at φ = 0.2, indicating that a large fraction of the dye is adsorbed by the shrunk PNIPAM gels, and it gradually increases to reach the initial concentration of the dye for φ > 0.6. For higher THF contents, the concentration of Nile Red in the external solution is practically the same with the initial concentration of the dye before equilibration with the PNIPAM gels, indicating that no adsorption of the dye takes places under these conditions.

The percentage of the adsorbed over the total amount of Nile Red, calculated from the difference between the initial concentration of Nile Red and the actual concentration of Nile Red in the external solutions, after equilibration with the PNIPAM gels, is presented in the inset of Figure 6 as a function of the volume fraction of THF, φ. As seen, for φ > 0.6, namely when the solvent mixture is a good solvent for both PNIPAM and Nile Red no adsorption takes place. On the contrary, as φ decreases towards 0.2, the quality of the solvent for both PNIPAM gels and Nile Red gets worst. Under these conditions, apparently, the rather shrunk PNIPAM gel offers a more convenient less polar environment for Nile Red than the water-rich bulk solvent. It is worthy to note that about 80% of the dye is adsorbed by the PNIPAM gels, at φ = 0.2.

CONCLUSIONS

In the present study, the adsorption of Nile Red by PNIPAM gels from binary water/THF mixtures was investigated as a function of the volume fraction of THF, φ. For the water-rich mixtures, $0 \leq \varphi \leq 0.1$, the solubility problems of the dye do not allow a reliable analysis of the results. However, for higher THF contents, $\varphi \geq 0.2$, Nile Red is readily soluble in the binary water/THF mixtures and the possible adsorption of the dye by the PNIPAM gel could be evaluated as a function of φ. In fact, it was found that adsorption is significant in water-rich mixtures, exhibiting simultaneously cononsolvency abilities towards PNIPAM. Indeed, a strong adsorption (about 80% removal of the dye, under the experimental conditions applied) occurs at φ = 0.2. However, the adsorption abilities of the PNIPAM gels weaken as φ increases and the gels reswell, so that no adsorption of Nile Red is found for THF-rich binary solvents, $\varphi \geq 0.6$.

To our knowledge, this is the first time that an enhanced adsorption of a dye by a hydrogel is reported under cononsolvency conditions. While in the present study we focused at the adsorption behavior of this system at room temperature, it would also be of interest to follow the influence of temperature on these properties, based on the well-known thermosensitive character of PNIPAM in aqueous solution. These properties would possibly find application in several "smart" systems, for instance for the purification of water or for the detection/concentration of organic pollutants from waste water.

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