TRANSPORT OF DYES IN POLYELECTROLYTE-SURFACTANT HYDROGELS

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Abstract

Polyelectrolyte-surfactant mixtures are progressive systems studied for their potential use in numerous applications in daily life including delivery systems for pharmaceutics. Mixing polyelectrolytes with oppositely charged surfactant ions in aqueous media typically leads to a strong association providing a simple route for constructing ordered materials with a great scientific and application potential. In this study, the combination of cationized dextran with sodium dodecylsulphate as surfactant was used for the preparation of two types of hydrogels. The diffusion of Nile red and Atto 488 dyes from their solutions in surfactant or NaCl into the hydrogels was monitored in time. The time development of the diffusion flows was used for the determination of basic transport characteristics of hydrogels. The diffusion of the probe dyes in prepared hydrogels was compared and discussed.

Keywords: Hydrogel, surfactant, polyelectrolyte, dye, diffusion

1. INTRODUCTION

Hydrogels are widely used for drug delivery systems in medicine of its unique characteristics [1-4]. These materials can prolong drug action and reduce side effects [1,5,6]. One of the main problems is how to solubilize hydrophobic compounds in hydrogels. The incorporation of some hydrophobic domains in the hydrogel structure would provide its solution. Hydrogels with the domains can be prepared by the interactions of polyelectrolytes with oppositely charged surfactant ions [4,7,8]. In this work, cationized dextran was used as polyelectrolyte and sodium dodecyl sulfate (SDS) as surfactant. Dextran is a bacterial-derived polysaccharide consisting of α-1,6-linked D-glucopyranose residues, and generally produced by enzymes from certain strains [9]. It is non-toxic and offers high water solubility, biocompatibility, and biodegradability. The strong interactions between dextran and SDS were observed [10] and it was driven by the interaction between the bile acid moiety and the surfactant [11]. Therefore their combination can be suitable for the preparation of hydrogel with domains capable to solubilize hydrophobic substances. Recently published results showed that the adsorption capacity of hydrogel for murexide increased with increase in contact time and initial dye concentration [12]. Other work confirmed the electrostatic interaction and hydrogen bonding between ibuprofen and dextran which had positive effect on its flowability, tableting and dissolution characteristics [13].

In this work, the incorporation of two different dyes into hydrogels based on dextran and SDS was studied. The aim is to describe absorption capacity and capability to absorb dyes by the diffusion from their solutions into prepared hydrogel. The dyes were used for the incorporation into domains prepared in the hydrogels.

2. MATERIALS AND METHODS

In this work, cationized dextran was used as polyelectrolyte. Diethylaminoethyl-dextran hydrochloride (Sigma-Aldrich, Czech Republic; DEAED) was used in one molecular weight 729 $\pm$ 3 kDa. Sodium dodecyl sulfate (SDS, ≥ 99.0 %) was purchased from Sigma Aldrich (Czech Republic) and used as surfactant.

All solutions were prepared in 0.15M NaCl solution using purified water (Purelab ELGA system). Salt solution was used because preliminary experiments showed that a non-zero ionic strength of the aqueous medium is important for obtaining gel-like materials [14]. Samples were prepared by mixing polyelectrolyte and surfactant stock solutions in a 1:1 volume ratio. The concentrations of initial solutions of polyelectrolyte and surfactant are given in **Table 1**.

Table 1 Concentrations of initial solutions used to prepare hydrogels

Sample	Dextran (wt%)	SDS (mM)
D-I	4	400
D-II	4	100

Nile red and Atto 488 (both purchased from sigma Aldrich) were dissolved in SDS (400mM for D-I and 100mM for D-II) or physiological saline (0.15M NaCl). The dyes were used in ten different initial concentrations listed in **Table 2**. Hydrogels were equilibrated (24 h), separated from the liquid residue by centrifugation at 4000 rpm for 15 min and covered by 5 cm^3 of SDS or NaCl solution with dissolved dye. The concentration decrease of dyes in solution was monitored by means of UV/VIS spectrometry (Hitachi U-3300). The data were used for the determination of dye absorption in hydrogels [15,16] distribution coefficient [16,17] and their diffusivity [15-18].

Table 2 Initial concentrations of dyes in the solutions of SDS and NaCl used for diffusion experiments

Solution	a	b	c	d	e	f	g	h	i	j
Dye (μM)	0.1	0.3	0.5	0.7	0.8	0.9	1.0	3.0	5.0	7.0

3.   RESULTS AND DISCUSSION

In this work, two different approaches for the investigation of transport of model dyes into hydrogels were applied. Nile red was prepared as its solution in SDS. The used concentrations of SDS were much higher than its critical micellar concentration (~8 mM) [19,20]. The aggregation number of SDS can be usually found between 40 and 70 [20,21], therefore the dye should be completely distributed in the micelles of SDS. In contrast, Atto 488 was dissolved in water and therefore we assumed that it diffused in hydrogels in the form of simple (partially dissolved) molecules. The theoretical ratio of charges between SDS and cationized dextran is ~4.6 for D-I and 1.2 for D-II. We assume that a part of SDS can be exhausted for the formation of hydrogel networks. In the case of D-I, this part is relatively small, therefore the pore structure in hydrogel contains solution with SDS micelles. In contrast, the large amount of SDS is consumed for the cross-linking of hydrogel D-II and the content of SDS in the pores is low. If we take account of these differences in the two used hydrogels, we can assume the faster diffusion into hydrogel D-II.

The examples of kinetic data are shown in **Figure 1**. We can see that the amount diffused into D-II hydrogels is higher for both used dyes. The dye content in hydrogels increased strongly mainly in first days. The rate of diffusion was strongly influenced by initial concentration of dye solution used as the source of diffusion particles. The concentration dependence is presented in detail in **Figure 2**. If we compare data obtained for Atto 488 and Nile red, we can say that the transport of Nile red into hydrogels is generally slower. Results published by Zhang et al. [22,23] showed that the diffusion of Atto 488 is faster also in water. The diffusion into hydrogels are more difficult as a result of their intrinsic structure constituted by the hydrogel network and pore structure. Due to various curvatures of pores, the diffusion is strongly influenced not only by the porosity (volume of pores) but also by tortuosity given by their shapes. Hydrogel D-I contains much more SDS than D-II and its structure should be more cross-linked. Therefore the diffusion into the hydrogel D-I is more difficult and the properties of hydrogel has the strong influence.
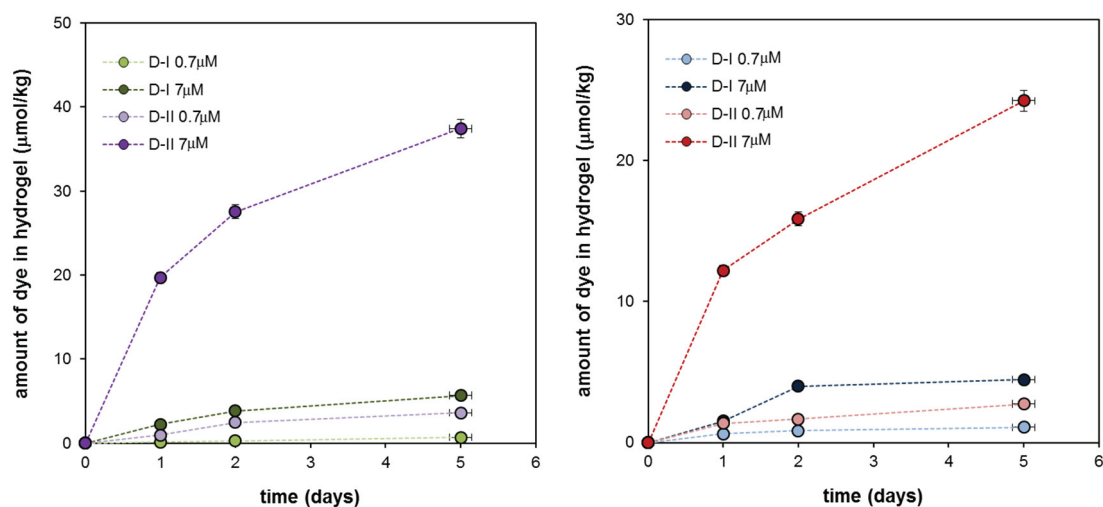
Figure 1 Kinetic data obtained for Atto 488 (left) and Nile red (right)
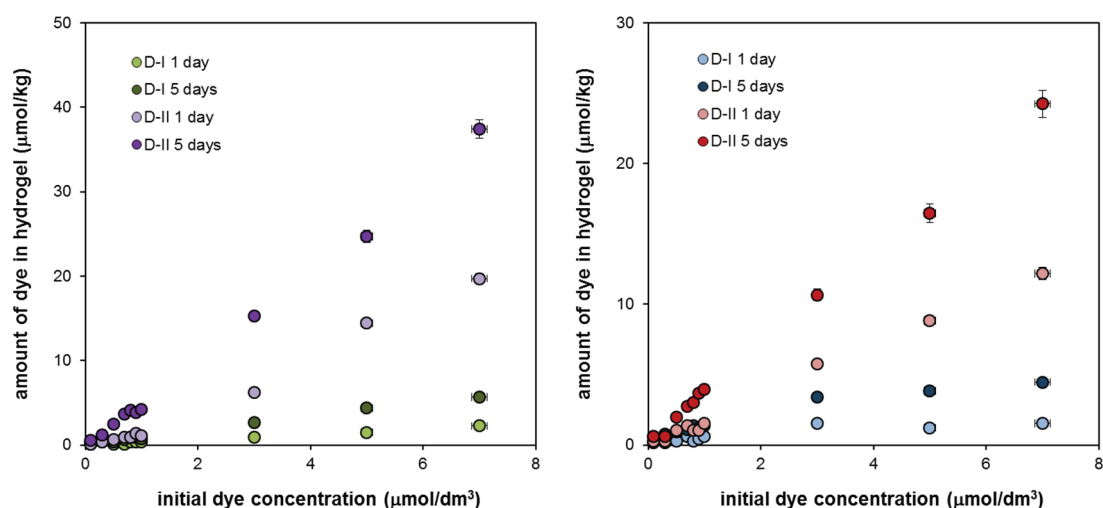

Figure 2 The amount of dyes diffused into hydrogels in the dependence on their initial concentrations: Atto 488 (left) and Nile red (right)

Maiti et al. [24] determined the diffusion coefficient of Nile red in SDS micelles. Its value (1.8×10^{-10} m²/s) was similar to our results for the diffusion of Nile red into D-II (Table 3). The values of effective diffusion coefficients listed in **Table 3** were obtained on the basis of mathematical model developed in our previous work [17]. This model was developed for the diffusion couple with phase interface. In this work, the couple is comprised by the hydrogel (acceptor part) and the solution of dye above hydrogel (donor part). Both parts are placed in cylindrical vessel. We can see that diffusion coefficients of Atto 488 in water (value published in ref. [22]) and the hydrogels are higher in comparison with results obtained for Nile red. The differences in results between both used dyes obtained for the hydrogel D-I are given mainly by two factors. The first one is the fact that Nile red was diffused in the form of micelles and the second one is the denser hydrogel network less accessible for the bigger particles. We assume that the influence of hydrogel structure can predominate in this case as was described above. In the case of Atto 488, other circumstance can affect the diffusion. The presence of high amount of SDS in the hydrogel D-I can lead to the incorporation of dye into micelles which conduced to the strong decrease of the diffusion coefficients.

Table 3 Effective diffusion coefficients of dyes in water and hydrogels

Medium	Atto 488	Nile red
water[a)]	4.0×10^{-10} m^2/s	3.3×10^{-10} m^2/s
D-I	1.5×10^{-10} m^2/s	1.1×10^{-10} m^2/s
D-II	2.8×10^{-10} m^2/s	1.5×10^{-10} m^2/s

a) published values: Atto 488 ref. [22], Nile red ref. [23]

Results obtained for the diffusion of both dyes into the hydrogel D-II are more different. The most of SDS was consumed for the cross-linking and the pore structure in the hydrogel D-II should be more accessible for the diffusion of dyes. We assume that the diffusion of Nile red into hydrogel D-II was strongly influenced by the fact that Nile red was transported as the micelles in SDS. It can cause the slowdown of diffusion both in water [24] and in the hydrogel. The size of diffusion particles is probably the main influencing factor in the diffusion into the hydrogel D-II.

The structural factor of hydrogels defined in our previous work [22] is the ratio between porosity and tortuosity. If no chemical reaction proceeds between hydrogel and dye the factor can be calculated as the ratio between diffusion coefficient of dye in hydrogel and in water. These factors are lower for Atto 488 (0.38 for the hydrogel D-I and 0.70 for the hydrogel D-II). In the case of Nile red, we used the diffusion coefficient publushed for Nile red in SDS micelles [24] for the calculation of the structure factor. The values of 0.61 (D-I) and 0.63 (D-II) were obtained.

4. CONCLUSION

The diffusion of two different dyes into the hydrogels based on the combination of cationized dextran with sodium dodecylsulphate as surfactant was studied. It was found that the incorporation of dyes into hydrogels is influenced by several factors. Nile red was used in the form of its micelles in SDS thus its transport into hydrogel network was more difficult. The diffusion of Atto 488 was affected by the presence of SDS into the pore structure in hydrogel D-I and its micelles can be formed during its transport. The diffusion coefficient of Atto 488 in the hydrogel D-II (which contained only small amount of SDS non-consumed for the cross-linking) was much faster.

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