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Interfacial Solubilization of Model Amphiphilic Molecules in Block Copolymer Micelles

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Abstract: We investigate the solubilization of 2-nitrodiphenylamine, a hydrophobic but polar dye molecule, in aqueous solutions of polystyrene$_{310}$-*b*-poly(acrylic acid)$_{47}$ micelles. The solubilization capacity of the micelles, which consist of a polystyrene core and poly(acrylic acid) corona, and the micelle−water partition coefficient are evaluated as a function of the solubilizate concentration. The solubilization isotherm shows a nonlinear behavior, and the partition coefficient, instead of being constant, is strongly dependent on the dye concentration. These results are explained by treating solubilization as a binding process, and by fitting the data to a Langmuir adsorption model. In addition, we examine the locus of solubilization of 2-nitrodiphenylamine using its solvatochromic properties and solubility in model solvents, and we identify the micellar interface as the solubilization site. Confirmatory studies, including the dependence of solubilization on the interfacial area of the aggregates, the role of the poly(acrylic acid) corona chains in stabilizing the solubilized molecules, and the effect of the solubilizate structure on the extent of incorporation, were also conducted. The results, consistent with surface localization, show that solubilization is dependent on the interfacial area of the aggregates, and on the affinity of the solubilizate for the micellar interface.

1. Introduction

It is well known that amphiphilic block copolymers, when dissolved in a solvent selective for one of the blocks, can self-assemble into aggregates of various morphologies, including spherical micelles.[1−15] If prepared in an aqueous medium, block copolymer micelles consist of a hydrophobic core surrounded by a hydrophilic corona. Reverse micelles, on the other hand, can be prepared in nonpolar solvents, in which case the hydrophilic chains constitute the micelle core, and the hydrophobic chains form the corona. An important property of micelles is their ability to enhance the solubility of insoluble, solvophobic small molecules, by trapping them in energetically compatible microenvironments.[16,17] For example, in aqueous media, the micelle hydrophobic core provides a microenvironment suitable for the incorporation of nonpolar, poorly water-soluble compounds. On the other hand, in nonpolar solvents, the hydrophilic core solubilizes polar molecules such as water, proteins, and amino acids.[18,19] The incorporated molecules are called solubilizates, and the related phenomenon is known as solubilization.[17,20]

The process of solubilization has been studied extensively in aqueous[21−27] and nonaqueous[28,29] solutions of conventional surfactants, as well as in solutions of block copolymer aggregates,[30−35] and has found a number of practical applications

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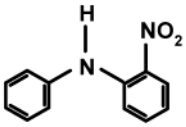
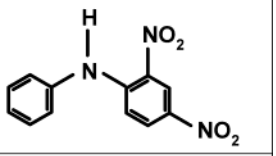
in fields such as drug delivery,[36−40] separation, toxic waste removal, and others.[20] Experimental and theoretical[16,41−43] studies have focused on determining the factors that control the solubilization capacity,[17,20,44] which is frequently expressed in terms of the micelle−water partition coefficient. Several factors have been identified, including the compatibility between the solubilizate and the core forming polymer,[2,45,46] the solubilizate molecular volume, and the interfacial tension between the solubilizate and water,[20,45] in addition to factors that affect the micelle size and aggregation number, such as the block copolymer composition,[41,42,46−48] molecular weight,[42,46,47] and the solution temperature.[17,49,50] A brief discussion of these factors is given in the Supporting Information.

In addition to identifying factors that control the solubilization capacity, several studies were dedicated to the determination of the solubilization site. The location of incorporated molecules within a micelle determines the extent of solubilization, the chemical reactivity of the solubilizates,[26] as well as the rate of their release from the micelles.[51] It is also a measure of the strength of specific interactions between the solubilizate and the micelle (hydrophobic, hydrogen bonding, van der Waals, etc). Several experimental methods such as NMR,[26,52] UV−vis spectroscopy,[52−54] fluorescence,[30,51,55,56] phosphorescence,[31] and solubility in model solvents,[52] as well as a few theoretical models,[57,58] have been employed to determine the locus of solubilization in surfactant and block copolymer micelles. The micelle can provide at least three thermodynamically distinguishable microenvironments for solubilization: the micelle core, the corona, and the core−corona interface. The highly nonpolar core is considered as the locus of solubilization for nonpolar molecules, such as alkanes.[2,24,45] For more polar solubilizates, such as ketones,[31] alcohols,[29,59] phenols, substituted phenols,[28,60,61] aniline, or anilinium ions,[26] the interfacial region is, generally, the solubilization site. The corona, on the other hand, is rarely involved in the solubilization of hydrophobic molecules. Mukerjee[57] has proposed one of the few theoretical models to predict the distribution of hydrophobic solubilizates (several benzoic acid derivatives) between the core and the corona of alkyl-oxyethylene micelles. It was assumed that the amount incorporated in the core, and in the corona, is proportional to the number of equivalents of the surfactant alkyl chain, and the surfactant oxyethylene group, respectively. Webber et al.,[51] who investigated the solubilization and release of pyrene and phenanthrene from block copolymer micelles, concluded that a significant fraction of the probe is present in an inner corona region, consisting of hydrophilic chains swelled with water, yet not accessible to ionic quenchers.[51]

Table 1. Structure and Properties of the Two Dyes Used

	
2-nitrodiphenylamine	2,4-dinitrodiphenylamine
MWt. = 214.22 g/mol	MWt. = 259.21 g/mol
Water solubility = 1.42 x 10^{-5} M	Water solubility = 1.97 x 10^{-5} M

Although the process of solubilization has been studied extensively in surfactant and block copolymer micelles, very few investigations were conducted as a function of the solubilizate concentration. In fact, most measurements were obtained in the presence of excess solubilizate, that is, at a single concentration corresponding to the maximum solubilization capacity of the micelles. Determining the extent of solubilization, or the micelle−water partition coefficient at different solubilizate concentrations, is essential for the fundamental understanding of the physicochemical aspects of the process of solubilization and, in many instances, for the accurate determination of the solubilization site. Also, such data are required to test the validity of theoretical models that treat solubilization in block copolymer aggregates.

In the present study, we investigate the solubilization of 2-nitrodiphenylamine, a hydrophobic but polar dye molecule, in aqueous solutions of polystyrene$_{310}$-*b*-poly(acrylic acid)$_{47}$ micelles, at various dye concentrations. 2-Nitrodiphenylamine was chosen as a model solubilizate because in preliminary experiments we found it to be solvatochromic; therefore, the sensitivity of its wavelength of maximum absorption, λ_{max}, to the microenvironment in which it is residing can be used to obtain information about its solubilization site. In addition, being a hydrophobic molecule with polar moieties (Table 1), its chemical structure resembles that of many drugs and biologically active molecules, such as hormones and steroids, making it an interesting model for drug-delivery applications. The micelles used are multimolecular, have an average aggregation number of ca. 260 chains/micelle, and a critical micelle concentration, cmc (estimated from similar systems),[62] of ca. 3×10^{-5}[9] (% w/w) in water. The solubilization capacity of the micelles and

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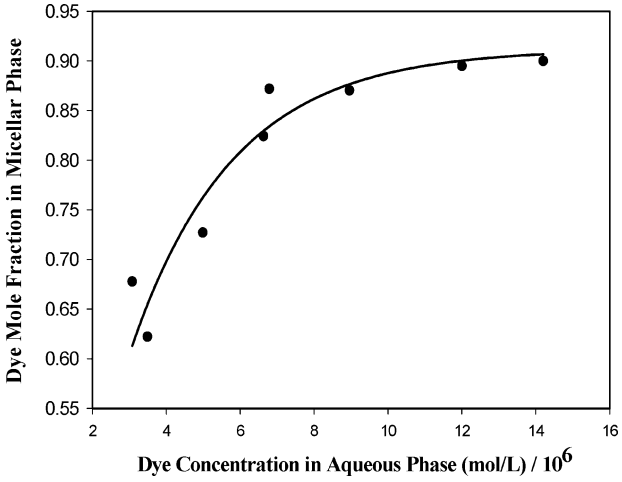

Figure 1. Solubilization isotherm of 2-nitrodiphenylamine in 0.26% w/w solutions of PS_{310}-*b*-PAA_{47}. The line is drawn only to guide the eye.

the micelle−water partition coefficient are evaluated as a function of the solubilizate concentration. The shape of the solubilization isotherm and the strong dependence of the partition coefficient on the dye concentration are explained by treating solubilization as an adsorption process, and by fitting the data to a Langmuir adsorption model. To the best of our knowledge, this is the first study that applies such a treatment to interpret solubilization in block copolymer micelles, and to explain the concentration dependence of the partition coefficient. In addition, we examine the locus of solubilization of the dye within the micelle using UV−vis spectroscopy and solubility in model solvents, and we identify the interfacial region as the solubilization site. The incorporation of 2-nitrodiphenylamine is also studied using aggregates of different diameters to determine the effect of the interfacial area on the amount incorporated, and in the presence of different concentrations of NaOH and HCl to evaluate the role of the poly(acrylic acid) corona chains in stabilizing the solubilized molecules. Finally, because the chemical structure of the solubilizate is expected to affect its affinity for the micellar interface and, consequently, the extent of its incorporation, we compare the maximum solubilization capacity of the micelles for 2-nitrodiphenylamine to that for 2,4-dinitrodiphenylamine, which is similar in structure, except for an additional nitro group present at the para position (Table 1).

2. Experimental Section

Experimental details are given in the Supporting Information.

3. Results and Discussion

3.1. Solubilization of 2-Nitrodiphenylamine in Micelles. The incorporation of 2-nitrodiphenylamine into micelles of $polystyrene_{310}$-*b*-$poly(acrylic\ acid)_{47}$ was carried out as a function of the solubilizate concentration. Figure 1 shows the results of solubilization into 0.26% w/w micellar solutions. The range of dye concentrations investigated was limited at the lower end by the detection limit of the UV−vis spectrophotometer and at the upper end by the maximum solubilizing capacity of the micelles. As shown in Figure 1, the dependence of the degree of incorporation on the dye concentration is nonlinear, meaning that the solubilization efficiency is not uniform throughout the examined concentration range. The most efficient incorporation, characterized by a high slope in the solubilization curve, occurs over a region where the aqueous dye concentration ranges between ca. 3×10^{-6} and 7×10^{-6} mol/L. At higher concentrations, the extent of solubilization increases only slightly with the dye concentration and reaches a plateau. The maximum solubilization capacity of the micelles (at mole fraction = 0.90) corresponds to 60 mg of dye per gram of polymer. It should be noted that, because the molecular weight of the polymer is much higher than that of the dye, the numerical value of the mole fraction is high, but the weight fraction of the dye solubilized in the micelles is considerably lower.

If the solubilization of hydrophobic molecules into micelles present in an aqueous solution is treated as the partitioning of the solubilizate molecules between two phases, an aqueous phase and a micellar phase, then, and similar to the case of partitioning between two bulk solvents, the partition coefficient should be constant and independent of concentration. Therefore, one would expect a plot analogous to that shown in Figure 1 to be linear. However, treating solubilization as a simple partitioning between two phases is not always a valid approach, because specific interactions between the micelles and the solubilizate can dominate the process of solubilization and result in a nonideal behavior, similar to the one reported above. Among the numerous studies that investigated the solubilization of hydrophobic molecules in block copolymer micelles, only few evaluated the partition coefficient as a function of the solubilizate concentration. Schechter et al.[46] investigated the solubilization of toluene in poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) micelles and reported a strong dependence of the partition coefficient, *K*, on the toluene concentration. Initially, *K* increases with the solubilizate concentration because the addition of toluene promotes aggregation, and solubilization is correspondingly promoted. With a further increase in the toluene concentration, *K* reaches a maximum and then decreases. The incorporation of toluene is considered to occur through the replacement of the water molecules present in the poly(propylene oxide) core. As more toluene is solubilized, it becomes more difficult to displace the remaining water from the core; therefore, solubilization becomes more restricted, and the partition coefficient decreases. Using surfactant micelles, Rouse et al.[63] and Christian et al.[59,61,64] studied the solubilization of slightly polar molecules as a function of the solubilizate concentration and showed that the partition coefficient decreases as the mole fraction of the solubilizate present in micelles increases. The moderately polar solubilizates investigated, which include hexanol and chloro-substituted phenols, fill sites in the palisade layer of the micelle in a fashion similar to surface adsorption. As the concentration of the incorporated solubilizate increases, the availability of such adsorption sites decreases, causing a decrease in the partition coefficient.

In the next section, we evaluate the micelle−water partition coefficient and analyze its dependence on the dye concentration. The nonlinear behavior of the solubilization isotherm shown in Figure 1 and the resulting dependence of the partition coefficient on the solubilizate concentration are explained by treating the solubilization of 2-nitrodiphenylamine as an adsorption process,

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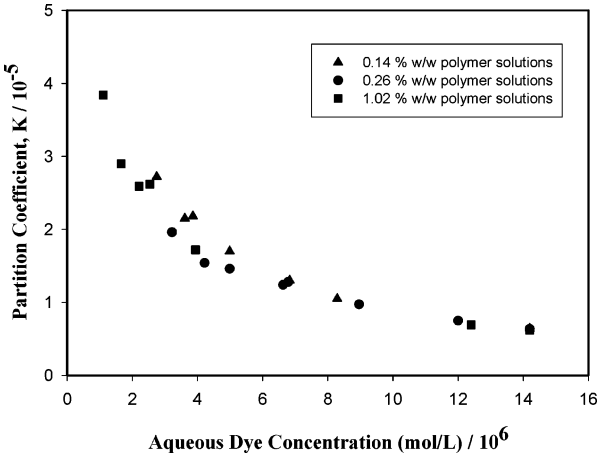

Figure 2. Partition coefficient of 2-nitrodiphenylamine between micelles of PS_{310}-*b*-PAA_{47} and water.

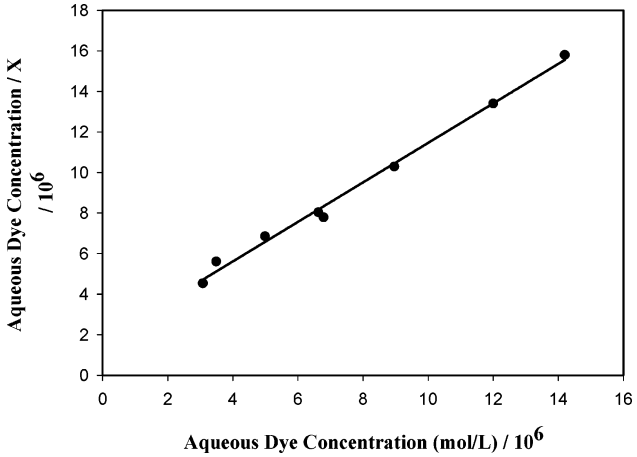

Figure 3. Langmuir adsorption isotherm for 2-nitrodiphenylamine in 0.26% w/w solutions of PS_{310}-*b*-PAA_{47}.

and by fitting the solubilization data to a Langmuir-type adsorption isotherm.

3.2. The Micelle−Water Partition Coefficient. The partition coefficient is a thermodynamic parameter that represents the affinity of a given solubilizate to the micellar phase, relative to the aqueous one. For practical applications, such as drug delivery, the micelle−water partition coefficient is used to determine the amount of drug molecules solubilized by the micelles, and to define the stability of the drug−micelle complex against dilution. In the present system, the partition coefficient, *K*, was evaluated for a series of PS_{310}-*b*-PAA_{47} micellar solutions, solubilizing different concentrations of 2-nitrodiphenylamine. The results, summarized in Figure 2, show that the partition coefficient is strongly dependent on the solubilizate concentration. The decrease of the partition coefficient with the dye concentration indicates that solubilization is a competitive process that becomes progressively more difficult as the amount of the dye incorporated into the micelles increases. This behavior is consistent with an adsorption-like phenomenon, which is possible considering that 2-nitrodiphenylamine is a polar molecule, capable of adsorbing at the micellar interface. Some researchers who studied solubilization in surfactant micelles used an adsorption approach to interpret the solubilization data.[19,65−67] For example, Patel and Kostenbauder,[65] who evaluated the degree of association between methyl *p*-hydroxybenzoate and Tween 80 molecules (polyoxyethylene 20 sorbitan monooleate), concluded that the solubilization of methyl *p*-hydroxybenzoate by Tween 80 occurs through binding and used a Langmuir-type adsorption model to interpret the data. Donbrow et al., who investigated the solubilization of hydroxybenzoic acids[67] and benzoic acid[66] in micelles of polyoxyethylene glycol monoalkyl ethers, also treated the solubilization as the binding of solubilizate molecules to specific sites in the micelles. They used a Langmuir isotherm to fit the data[66,67] and concluded that the micelle interface is the adsorption site in the case of benzoic acid,[66] while in the cases of meta- and para-hydroxy acids, it is the polyoxyethylene corona.[67] For the present system, we fitted the solubilization data to several adsorption models and found that the data best fit a Langmuir adsorption isotherm. The fit to other adsorption models is given in the Supporting Information. The general equation for a Langmuir-type adsorption can be expressed as:[68]

$$\frac{x}{x_{\max}} = \frac{K_{\mathrm{ad}}C}{1 + K_{\mathrm{ad}}C}$$

where x, $x_{\max}$, K_{ad}, and C are the solubilizate mole fraction in the micellar phase, the maximum of that mole fraction, the adsorption constant, and the molar concentration of free, unbound dye molecules, respectively. Upon rearrangement, the above equation becomes

$$\frac{C}{x} = \frac{1}{K_{\mathrm{ad}}x_{\max}} + \frac{C}{x_{\max}}$$

The plot of C/x versus C, given in Figure 3, is in fact linear, with $R^2 = 0.993$, showing that the solubilization data fit the Langmuir adsorption model. The values of $x_{\max}$ and K_{ad} determined from the slope and intercept of the plot are 1.03 ± 0.03 and $(5.7 \pm 1.0) \times 10^5$ L/mol, respectively. Reported values of the Langmuir adsorption constant vary depending on the nature of the substrate and the adsorbate. For example, the values reported for the adsorption of cationic surfactant molecules on poly(acrylic acid) brushes range from 7×10^2 to 3×10^6 L/mol,[69] and for the adsorption of benzoic acid to micelles of polyoxyethylene glycol monoalkyl ethers, they range from 18 to 34 L/mol.[67]

3.3. The Locus of Solubilization within the Micelles. Although the applicability of a Langmuir-type treatment to the solubilization of a hydrophobic yet polar molecule such as 2-nitrodiphenylamine implies surface localization, it is important to confirm this assignment using independent methods. Preliminary experiments showed that 2-nitrodiphenylamine is solvatochromic; that is, its wavelength of maximum adsorption is sensitive to the microenvironment in which it is residing. Therefore, information about the locus of solubilization can be obtained by comparing $\lambda_{\max}$ of the dye in micellar solutions to that in model solvents that mimic the polarity of different regions of the micelle. In addition, by calculating the total interfacial

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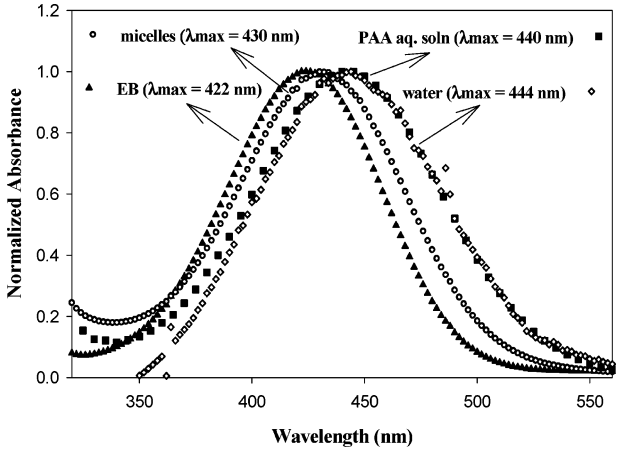

Figure 4. Normalized absorption spectra of 2-nitrodiphenylamine in different solutions.

Table 2. The Wavelength of Maximum Absorption, and the Full-Width at Half-Height of 2-Nitrodiphenylamine in Different Solutions

	ethylbenzene	micelles	poly(acrylic acid) aqueous solution	water
λ_{max} (nm)	422	430	440	444
fwhh	82	88	95	96

area of the micelles, one can determine if sufficient area is available for the surface localization of the solubilized dye molecules. Finally, using model solvents, we could estimate the possible solubilizing capacity of the micelle core and corona. By comparing these capacities to the experimentally determined solubilization capacity of the micelles, we can determine if the micelle core or corona can accommodate the amount of dye found to be incorporated in the micelles, and, therefore, if they are possible solubilization sites. The results of these investigations are discussed in the following sections.

3.3.1. Shift in the Wavelength of Maximum Absorption, λ_{max}. Block copolymer micelles can offer at least three different sites for solubilization: the micelle core, its corona, and the core−corona interface. Information about the solubilization site of 2-nitrodiphenylamine within the micelles was obtained by comparing its wavelength of maximum absorption (λ_{max}) in a micellar solution to that in ethylbenzene, in an aqueous solution of poly(acrylic acid) and in water. Ethylbenzene was chosen to mimic polystyrene, the micelle core-forming block, because of the similarity in structure and polarity, while the aqueous solution of poly(acrylic acid) was chosen to represent the polarity of the micelle corona, which consists of poly(acrylic acid) chains swelled with water. In Figure 4, we show the normalized absorption spectra of 2-nitrodiphenylamine in these four different systems, and, in Table 2, the corresponding values of the wavelength of maximum absorption, λ_{max}, and the full-width at half-height, fwhh, are given. When solubilized in the micelles, 2-nitrodiphenylamine absorbs at $\lambda_{max} = 430$ nm, which is intermediate in value between λ_{max} in ethyl benzene ($\lambda_{max} = 422$ nm) and that in an aqueous solution of poly(acrylic acid) ($\lambda_{max} = 440$ nm). Such a shift in the wavelength of maximum absorption indicates that the solubilized dye molecules are residing in a microenvironment of intermediate polarity as compared to ethylbenzene and aqueous poly(acrylic acid). However, it is also conceivable that the absorption band in the micellar solution is a superposition of two unresolved peaks, one representing the absorption in the micelle core, which is an ethylbenzene-like environment, and the second representing the absorption in an aqueous poly(acrylic acid)-like environment, which represents the micelle corona. This possibility is eliminated because the values of fwhh indicate that the absorption peak in the micellar solutions is not sufficiently broad to be considered a superposition of the peak in ethylbenzene and that in aqueous poly(acrylic acid) solution. In addition to the information obtained from the fwhh, the first derivative of the absorption spectrum in micellar solution was determined and compared to that in ethylbenzene and in an aqueous solution of poly(acrylic acid) (Figure 1 in the Supporting Information). The shape of the first derivative curve was identical in the three systems, with a single inflection point, indicating that absorption in micellar solutions is, in fact, a single peak. The dye molecules, therefore, once solubilized by the micelles, are residing in a single environment, and the polarity of such an environment is intermediate between that of ethylbenzene, on one hand, and aqueous poly(acrylic acid), on the other. These results suggest the micellar interface as the most reasonable solubilization site for the hydrophobic, but polar, molecules of 2-nitrodiphenylamine. Solubilization at the interface would allow the polar groups of the dye molecules to interact with the exterior aqueous solution, and possibly with the acrylic acid chains, while at the same time maintaining the possibility of hydrophobic interactions between the nonpolar parts of the dye molecules and the polystyrene core of the micelles.

3.3.2. Total Interfacial Area of the Micelles. In this section, we determine if sufficient micellar surface area is available for the interfacial localization of the solubilized dye molecules. To do so, we estimate the area of one dye molecule (using a molecular model) and compare the area required to accommodate all of the dye molecules incorporated at saturation to the total surface area of the micelles. The micelles have an average diameter of ca. 30 nm, as determined by transmission electron microscopy. This number includes both the polystyrene core and the poly(acrylic acid) corona. The micellar surface area, calculated on the basis of the radius of the polystyrene core, is ca. 2.8×10^3 nm^2/micelle, and the average aggregation number, estimated from the volume of polystyrene per micelle, is about 260 chains/micelle. The details of these calculations are given in the Supporting Information. Therefore, in 1 g of a 1.0% w/w solution of these micelles, the total number of micelles is ca. 6.5×10^{14}, and the total micellar surface area is ca. 1.8×10^{18} nm^2. At saturation, the number of dye molecules solubilized by the micelles was found to be ca. 1.4×10^{18} molecules/g of solution. Because the estimated area of one dye molecule is ca. 0.77 nm^2, the incorporation of all of the dye molecules would require an area of 1.0×10^{18} nm^2, which corresponds to ca. 60% of the total micelle interfacial area. It should be recalled that the chains of acrylic acid extending from the surface of the micelles also occupy part of the surface area. We have estimated the area per corona chain to be ca. 0.5 nm^2 (details given in the Supporting Information). For an aggregation number of 260 chains/micelle, the corona chains occupy ca. $260 \times 0.5 \times 6.5 \times 10^{14} = 8.4 \times 10^{16}$ nm^2/g solution, or ca. 5% of the total surface area. These approximate calculations show that the micellar interface can, indeed, accommodate the number of dye molecules solubilized even at saturation, at which point the surface is approximately 65% covered. Considering that the dye

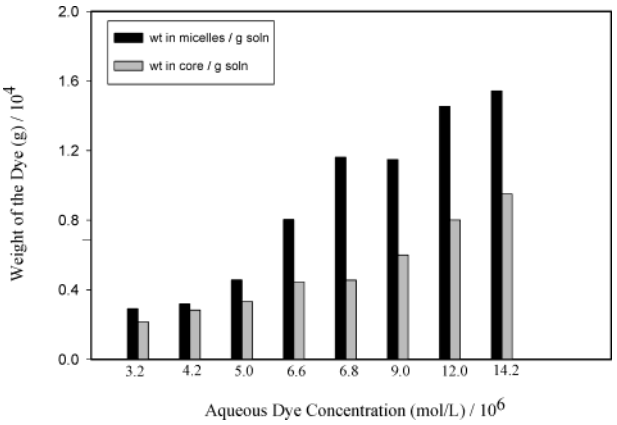

Figure 5. Comparing the weight of 2-nitrodiphenylamine possibly present in the core (calculated) to the experimentally determined weight solubilized by the micelles.

molecules are not expected to pack on the surface with a crystal-like precision, and that the emanating poly(acrylic acid) chains represent a significant perturbation to the packing efficiency, a 65% coverage at saturation does not seem unreasonable.

3.3.3. Solubility in Model Solvents. The analysis of the absorption spectra discussed previously shows that the solubilization of 2-nitrodiphenylamine occurs in a single site. The shift in λ_{max} suggests the micellar interface as the locus of solubilization, and the calculations of the available micellar interfacial area show that the interface can accommodate the amount of dye molecules solubilized. In this section, we estimate the solubilization capacity of the micelle core and corona using model solvents and show that neither one can accommodate the total amount of dye incorporated, further supporting the proposed micelle interface as the locus of solubilization.

The solubilizing capacity of polystyrene, which constitutes the micelle core, was estimated using ethylbenzene as a model solvent. The ethylbenzene−water partition coefficient, calculated using eq 2 of the Supporting Information as $K_{EB/H_2O} = 1.3 \times 10^4$, was used to determine the amount of the dye molecules that can possibly be present in the polystyrene core for a given amount of the dye present in the aqueous phase. Calculations were done for a series of 0.26% w/w micellar solutions of polystyrene$_{310}$-*b*-poly(acrylic acid)$_{47}$, solubilizing different concentrations of 2-nitrodiphenylamine. In Figure 5, we summarize the results of these calculations and compare the calculated weight of the dye possibly present in the polystyrene core to the experimentally determined weight solubilized by the micelles. For example, at saturation (the far right in Figure 5), in 1 g of the 0.26% w/w micellar solution, the weight of polystyrene is ca. 2.4×10^{-3} g, and the aqueous dye concentration is 1.4×10^{-5} mol/L. Using eq 2, and the above value of the ethylbenzene−water partition coefficient, the number of moles of the dye possibly present in the polystyrene phase is ca. 4.4×10^{-7} mol (9.5×10^{-5} g). However, experimentally, the micelles contain ca. 7.2×10^{-7} mol (1.5×10^{-4} g) of 2-nitrodiphenylamine. This means that the weight of polystyrene present in the system cannot completely account for the amount of 2-nitrodiphenylamine solubilized by the micelles. As can be seen in Figure 5, this observation applies not only at saturation, but also for solutions solubilizing smaller concentrations of the dye. Therefore, while the spectroscopic data suggest that the dye molecules are residing in a single environment where the polarity is intermediate between that of ethylbenzene and aqueous poly(acrylic acid), the above calculations show that this environment is not likely to be the polystyrene core.

Considering that the polystyrene core has a certain affinity for the dye molecules, the extent of which is reflected by the value of the ethylbenzene−water partition coefficient, one might expect the incorporation of the dye molecules to occur, in addition to the interface, inside the micelle core as well. For instance, one can speculate that with increasing dye concentrations, and as the micellar interface saturates its capacity for incorporation, the polystyrene core would participate in the solubilization of the dye molecules. This would be reflected by a shift in λ_{max} of the dye in micellar solution with the extent of solubilization. In the present system, however, no such shift was observed, and the wavelength of maximum absorption of the dye in micellar solution was independent of the dye concentration, indicating that solubilization occurs in the same site for all of the examined degrees of incorporation. A similar behavior was observed during the solubilization of anilinium cations in sodium dodecyl sulfate micelles.[26] The researchers used NMR spectroscopy to determine the locus of solubilization and concluded that the anilinium ion is located at the micellar interface and does not penetrate into the micellar core even at high concentrations. Such a behavior was attributed to the polar characteristic of the solubilized ion.

The maximum solubilizing capacity of the micelle corona, which consists of poly(acrylic acid) chains swelled with water, was estimated using an aqueous solution of poly(acrylic acid) as a model solvent. We have determined the amount of the dye solubilized by a 9.5% w/w aqueous solution of poly(acrylic acid) at saturation, that is, when the aqueous dye concentration corresponds to its solubility limit. The maximum weight of the dye interacting with acrylic acid (calculated from the total weight of the dye in solution minus the weight present in water) was approximately 4.2×10^{-4} g of dye/g of acrylic acid. Therefore, in a 1 g solution of 0.26% w/w PS$_{310}$-*b*-PAA$_{47}$, which contains 2.5×10^{-4} g of acrylic acid, the maximum weight of the dye that can be solubilized by acrylic acid corona is ca. 1.0×10^{-7} g. However, and as discussed previously, in a 1 g solution of 0.26% PS$_{310}$-*b*-PAA$_{47}$, the micelles incorporate 1.5×10^{-4} g of the dye. Therefore, the contribution of poly(acrylic acid) to solubilization is small (ca. 0.07%); consequently, the micelle corona cannot be the solubilizing site for 2-nitrodiphenylamine molecules.

Determining the solubility of 2-nitrodiphenylamine in model solvents shows that neither the polystyrene core of the micelles nor the poly(acrylic acid) corona can completely accommodate the amount of dye solubilized at any of the investigated degrees of loading. These results, coupled with the calculations of the available micellar surface area and the shift in the wavelength of maximum absorption, indicate that the solubilization of the dye molecules occurs at the micelle interface.

3.4. Solubilization as a Function of Interfacial Area. The interfacial solubilization of 2-nitrodiphenylamine would mean that the extent of incorporation is dependent on the total interfacial area of the aggregates, rather than the weight of polystyrene, which constitute the micelle core. To test this hypothesis, we evaluate the maximum amount of dye solubilized (i.e., solubilization at saturation) as a function of the interfacial area, while keeping the total weight of polystyrene in solution

Table 3. Solubilization of 2-Nitrodiphenylamine (2NDPA) as a Function of the Aggregates' Interfacial Area

polymer	aggregates	avg. diam (nm)	interf. area (outer only) (nm^2)	interf. area (outer + inner) (nm^2)	2-NDPA (m·mol)
PS_{310}-*b*-PAA_{47}	micelles	30	5.70×10^{17}	5.70×10^{17}	8.1×10^{-4}
PS_{310}-*b*-PAA_{45}	vesicles	100	1.50×10^{17}	1.79×10^{17}	5.8×10^{-4}
PS_{310}-*b*-PAA_{36}	vesicles	240	1.11×10^{17}	1.76×10^{17}	5.1×10^{-4}

Table 4. Comparing the Solubilization of the Two Dyes in 0.26% w/w Micellar Solution

	K_{EB/H_2O}	max wt. dye/wt. AA (g/g)	max wt. dye/wt. polym. (mg/g)
2-nitrodiphenylamine	1.3×10^4	4.2×10^{-4}	60.5
2,4-dinitrodiphenylamine	5.0×10^3	3.4×10^{-4}	9.4

constant. The interfacial area was varied by preparing aggregates of different diameters. The structures used for this experiment include 30 nm diameter micelles of PS_{310}-*b*-PAA_{47}, 100 nm diameter vesicles of PS_{310}-*b*-PAA_{45}, and 240 nm diameter vesicles of PS_{310}-*b*-PAA_{36}. Aqueous solutions of these three systems containing the same weight of polystyrene, ca. 2.4×10^{-3} g, were saturated with 2-nitrodiphenylamine, and the maximum solubilization capacity was determined per gram of solution. Note that, for vesicles, the interfacial area was calculated first for the external surface only, and second for both the external and the internal surfaces. The results, summarized in Table 3, show that the extent of solubilization is, in fact, related to the total interfacial area of the aggregates. The amount of 2-nitrodiphenylamine incorporated decreases with decreasing interfacial area, although the total weight of polystyrene remains constant. While the plot (not shown) is not linear, the trend is clear. The dependence of solubilization on the total surface area of the aggregates further supports the results obtained from UV−vis spectroscopy and solubility in model solvents and indicates that solubilization occurs at the micelle core−corona interface.

3.5. Effect of Additives on the Solubilization of 2-Nitrodiphenylamine. This work is presented in the Supporting Information.

3.6. Solubilization of 2,4-Dinitrodiphenylamine. The chemical structure of the solubilizate is expected to influence its affinity for the micellar interface and, consequently, the extent of its solubilization. Therefore, it was of interest to compare the maximum solubilizing capacity of the micelles for 2-nitrodiphenylamine to that for 2,4-dinitrodiphenylamine. As shown in Table 1, the two molecules have a similar chemical structure, except for the presence of an additional nitro group at the para position in 2,4-dinitrodiphenylamine. Despite the structural similarity, the maximum solubilization of 2,4-dinitrodiphenylamine in PS_{310}-*b*-PAA_{47} micelles was approximately 10 mg of dye per g of polymer (Table 4), significantly lower than that of 2-nitrodiphenylamine (ca. 60 mg/g). As discussed previously, the location of such polar molecules at the micellar interface allows their nonpolar moieties to interact with the polystyrene core of the micelle and maintains, at the same time, a possible interaction between their polar groups and the external aqueous solution. Therefore, to explain the observed difference in incorporation, we consider the difference in the hydrophobicity of the two dyes, that is, in their affinity for the micelle core, and in their basicity, which would influence the hydrogen bonding between the amino group of the dye (the lone pair on the nitrogen) and water.

As a measure of their affinity to the polystyrene core, the ethylbenzene−water partition coefficient was evaluated for the two dyes. The results, given in Table 4, show that 2,4-dinitrodiphenylamine is less hydrophobic than 2-nitrodiphenylamine. It is also a slightly weaker base, as indicated by its weaker interaction with poly(acrylic acid) (Table 4). In addition to its weaker affinity for the micellar core and smaller tendency for hydrogen bonding, the location of 2,4-dinitrodiphenylamine at the micellar interface would expose the nitro group at the para position to the nonpolar environment of polystyrene, a thermodynamically unfavorable situation not encountered during the solubilization of 2-nitrodiphenylamine. The smaller hydrophobicity and basicity of 2,4-dinitrodiphenylamine and its weaker affinity for the micellar interface explain its lower degree of solubilization.

4. Summary and Conclusions

We have investigated the solubilization of 2-nitrodiphenylamine, a hydrophobic but polar molecule, in micelles of polystyrene$_{310}$-*b*-poly(acrylic acid)$_{47}$. Using the equilibrium dialysis method and UV−vis spectroscopy, we determined the extent of incorporation as well as the micelle−water partition coefficient as a function of solubilizate concentrations. The solubilization isotherm showed a nonlinear behavior, and the partition coefficient, instead of remaining constant, decreased with the solubilizate concentration, indicating that solubilization occurs in an adsorption-like manner. The solubilization data were therefore treated using different adsorption models and showed a best fit to the Langmuir adsorption isotherm. To the best of our knowledge, this is the first study that uses an adsorption approach to treat the solubilization of hydrophobic molecules in block copolymer micelles and to explain the concentration dependence of the partition coefficient. While the applicability of the Langmuir formalism for the solubilization of such a hydrophobic molecule implies surface localization, it was important to confirm the locus of solubilization independently.

Information about the solubilization site was obtained by analyzing the absorption spectra of 2-nitrodiphenylamine in solutions that mimic the polarity of different parts of the micelle. The results indicated that the solubilization occurs in a site of intermediate polarity between ethylbenzene and aqueous poly(acrylic acid), consistent with interfacial localization. Evaluating the total interfacial area of the micelles showed that the interface could, indeed, accommodate the amount of dye solubilized, even at saturation. Finally, determining the possible solubilizing capacity of the micelle core and corona using model solvents showed that neither one can completely account for the amount solubilized at any given degree of loading, further supporting the proposed interfacial solubilization.

Solubilization at the micellar interface implies that the extent of incorporation is dependent on the interfacial area of the aggregates, rather than the volume of the micelle core. To test this hypothesis, we determined the maximum solubilizing capacity of the block copolymer aggregates as a function of their interfacial area, and the results, consistent with our predictions, indicated that the extent of solubilization decreases

with a decrease in the interfacial area, even though the weight of polystyrene remained constant. In addition, we measured the maximum solubilizing capacity of the micelles in the presence of different concentrations of NaOH and HCl, that is, at different degrees of dissociation of poly(acrylic acid). The aim was to determine to what extent are the poly(acrylic acid) corona chains involved in stabilizing the dye molecules incorporated at the micelle interface. Because the amount incorporated was independent of NaOH or HCl concentration, we concluded that the interactions between the amine group of 2-nitrodiphenylamine and the carboxylic acid groups of poly(acrylic acid), although possible, are not a major contributor to the stabilization of the dye molecules located at the interface. Finally, the solubilization of 2-nitrodiphenylamine was compared to that of 2,4-dinitrodiphenylamine to show that the affinity of the solubilizate to the micellar interface can control the extent of solubilization. The lower compatibility of 2,4-dinitrodiphenylamine with the polystyrene core and its smaller tendency for hydrogen bonding with the external aqueous solution, that is, its weaker affinity for the micellar interface, result in a significantly smaller degree of incorporation.

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Supporting Information Available: A brief literature review of the factors that affect the solubilization capacity, experimental details, the fit to different adsorption isotherms, the calculations of the micellar surface area, aggregation number and the surface area of a poly(acrylic acid) chain, the plot of the first derivative of the adsorption spectra of 2-nitrodiphenylamine, as well as the section discussing the effect of additives on solubilization (PDF) This material is available free of charge via the Internet at http://pubs.acs.org.

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