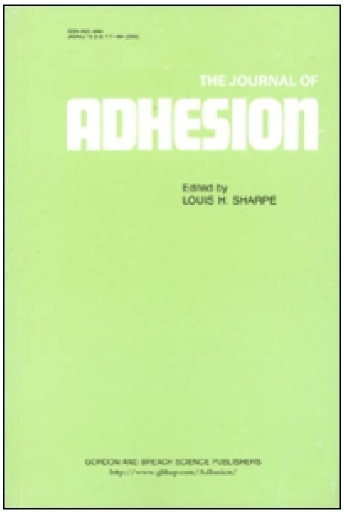

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ADSORPTION AND WETTING PROPERTIES OF PLURONIC BLOCK COPOLYMERS ON HYDROPHOBIC SURFACES STUDIED BY OPTICAL WAVEGUIDE LIGHTMODE SPECTROSCOPY AND DYNAMIC TENSIOMETRIC METHOD

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ADSORPTION AND WETTING PROPERTIES OF PLURONIC BLOCK COPOLYMERS ON HYDROPHOBIC SURFACES STUDIED BY OPTICAL WAVEGUIDE LIGHTMODE SPECTROSCOPY AND DYNAMIC TENSIOMETRIC METHOD

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Adsorption of four different poly(ethylene oxide)/poly(propylene oxide)/poly (ethylene oxide) triblock copolymers (Pluronics®) onto the hydrophobized surface of the sensor was measured by the optical waveguide lightmode spectroscopy (OWLS). Adsorbed amounts of Pluronic PE10300, PE10500, PE6400, and PE6800 determined in the concentration range of 10^{-2}–10 gdm^{-3} were found to follow the order of the hydrophobicity of the Pluronic compounds characterized by their hydrophil–lipophil balance (HLB) values. Wettability of two hydrophobic surfaces, the poly(lactide-co-glycolide), PLGA70/30 copolymer (used as drug carrier in pharmaceutical applications) and silylated glass, in aqueous solutions

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One of a collection of papers honoring A. W. Neumann, the recipient in February 2004 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

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of the above Pluronics were studied by a dynamic tensiometric method. The significant increase in the wetting tension observed after the adsorption of the surfactants, and hence the decrease of the apparent contact angle as the indication of the wetting effect on both the biopolymer and the hydrophobic glass, was correlated to the poly(ethylene oxide) (PEO) content of the adsorbed layer obtained on the hydrophobized sensor surface by the OWLS method.

Keywords: Dynamic wetting; Adsorption of Pluronics; Optical waveguide lightmode spectroscopy (OWLS); Surface-active block copolymers; Poly(lactide-co-glycolide) copolymer; Wetting tension

INTRODUCTION

Triblock poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide) (PEO-PPO-PEO) copolymers commercially available under the name of Pluronic® (BASF) are water-soluble, nonionic amphiphilic surfactants. The Pluronics with varying PPO and PEO block sizes are widely used in industrial applications from detergents to pharmaceutical additives. They are also well known surface modifiers for improving the stability of hydrophobic colloidal particles in aqueous media [1, 2]. These applications are based on surface activity, *i.e.*, the adsorption properties of the Pluronics at various air–water, liquid–liquid, or solid–water interfaces [3]. Due to the biocompatible character of PEO-containing coatings applied to various biomaterials, interest has focused on the properties of adsorbed Pluronic layers and their role in reducing nonspecific protein adsorption and cell adhesion on biomaterial surfaces [4–7].

The interfacial adsorption behavior of block copolymer surfactants from solutions has been extensively studied [8, 9]. Their amphiphilic nature arises from the different solubilities of the copolymer blocks. The adsorption behavior at air–water and hydrophobic solid–water interfaces shows similarity considering the polarities of the phases and hence the orientation of the various blocks at the interface. It is accepted that the hydrophobic PPO chains provide the necessary anchor for the polymer molecules to remain adsorbed at the interface, and the PEO chains extend into the solvent phase. To characterise quantitatively the adsorption of Pluronics at the solid–liquid interface, colloidal systems, latex, or other solid particles were used as model surfaces in previous works [1, 10–13]. For studies on macroscopic solid surfaces sensitive techniques such as ellipsometry [14, 15] or reflectometry [16] were required to monitor the adsorption process. As a related technique [17], optical waveguide lightmode spectroscopy (OWLS) is a convenient and versatile method for probing adsorption processes in real time and providing valuable information concerning the structure of the adsorbed layer (thickness and refractive index of the layer) [18, 19]. The integrated optical method is based on the measurement of polarizability density (*i.e.*, refractive index) in the vicinity of the waveguide surface. Measurement of two guided modes enables the absolute mass of adsorbed molecules to be determined. As an extremely surface-sensitive technique it has found many applications [20–23] in the analysis of biospecific, *e.g.*, antigen–antibody, interactions.

Despite the large amount of work considering the adsorption of Pluronics, little knowledge is available about the relationship of solid-surface adsorption to the wetting properties of certain Pluronic compounds. Our aim was to relate the chemical structure of the block copolymers and their adsorption behavior to their wetting effect on hydrophobic surfaces. In the present study the adsorbed amount of four Pluronics (PE10300, PE10500, PE6400, and PE6800) on a hydrophobic sensor surface was measured using the OWLS technique. These adsorption data were then correlated to the wetting effect of the same Pluronics on hydrophobized glass and a polymeric surface (poly(DL-lactide-co-glycolide), PLGA70/30) evaluated form the tensiometric contact angle measurements. The results that will be obtained by the two independent methods might provide a valuable practical guidance regarding the selection of the most effective Pluronic for increasing the wettability of the polymeric drug carrier of interest.

EXPERIMENTAL

Materials

PEO-PPO-PEO triblock copolymers (Pluronic,® provided by BASF Hungaria Kft., Budapest, Hungary) were applied without further purification in our experiments. The composition of four Pluronics, PE10300, PE10500, PE6400, and PE6800, with their selected physico-chemical parameters [24] are listed in Table 1. Trimethylchlorosilane (Fluka, Chemie AG, Buchs, Switzerland) was used to render the surfaces of both the OWLS sensor and the glass used for wettability measurements hydrophobic. PLGA70/30 (Mw: ~3000) random copolymer with 70% lactide and 30% glycolide content was obtained from Polysciences, Inc. (Warrington, PA, USA). Dichloromethane (p.a., ACS Grade, Merck, Darmstadt, Germany) was used as solvent for polymer film preparation. Doubly distilled water obtained from a Wagner and Munz Muldestor SE apparatus (München, Germany)

TABLE 1 Physico-chemical Parameters (Average Molecular Weight, Composition of Triblock Molecules, Critical Micellar Concentration, Hydrophilic–Lipophilic Balance, and Surface Tension Values at Concentration of 1 gdm^{-3}) of the Pluronic Compounds (Data Supplied by the Manufacturer or Taken from Reference Indicated)

Pluronic	$\bar{M}$	Composition mon.units	c_M[a] gdm^{-3} (mM)	HLB	γ mNm^{-1}	m_A 10^{-6}mol m^{-2}	A nm^2/molecule	d_A nm
PE10300	4950	17/56/17	0.7 (0.14)	9	34.4	0.73[b]	2.3	6.1
PE10500	6500	37/56/37	2.3 3.0[c] (0.35 0.46)	15	39.1	0.51	3.3	4.4
PE6400	2900	13/30/13	11–110 (3.8–38)	15	43.2	0.86	1.9	3.7
PE6800	8400	76/30/76	190 (22.6)	29	50.3	0.31	5.3	5.8

The adsorbed amount at bulk concentration of 10 gdm^{-3}, m_A, the corresponding molecular area, A, and the adsorption layer thickness, d_A, determined from OWLS measurements (present study) are also summarized in the last three columns.

[a] Chu and Zhou [25].

[b] Measured at concentration of 1 gdm^{-3}.

[c] Alexandridis *et al.* [26].

checked by its conductivity ($< 5\,\mu S$) and surface tension (>72.0 mN/m) was used for wettability measurements. Both the adsorption and the wettability measurements were carried out at 25 ± 0.2°C.

Substrates

OW Sensor

OW2400-type optical grating coupled waveguide sensor chips (Micro Vacuum, Budapest, Hungary) were used in the OWLS measurements. The OW2400 chip is based on a fine optical grating prepared on a thin waveguide layer carried by a glass substrate. The refractive index of the glass support and waveguiding film layer are 1.53 and 1.77, respectively. The grating periodicity is 2400/mm. The waveguide layer on the surface of the OW2400 sensor with a thickness of 170–220 nm is composed of 75% TiO_2 and 25% SiO_2. Since the TiO_2 like other metal oxides, are described to react with silylating agents [27], this surface layer was rendered hydrophobic by the same protocol, which was developed for treatment of the glass surfaces [28]. To remove any possible contamination, the sensor chips were cleaned in a sonicating bath for 10 min in ethanol and then water, two times in each.

The cleaned plates were silylated in the gas phase of trimethylchlorosilane in a closed chamber at 140°C for 2 h. After rinsing the surfaces with diethylether, ethanol (to remove physically absorbed silane molecules [29]), and water, subsequently, the samples were dried in a vacuum overnight.

Substrates for Wettability Measurements

Wettability measurements with water and the aqueous solutions of four Pluronic compounds applied at different concentrations were performed on PLGA70/30 and on hydrophobized glass surfaces. PLGA70/30 surfaces were prepared by dipping a freshly cleaned microscopic cover glass plate into 2 w/v% solution of the polymer in dichloromethane and slowly drying them for 30 min in order to obtain smooth and transparent surfaces. Then the polymer samples were kept in vacuum chamber for 24 h to let the solvent completely evaporate before their use for wettability measurements.

Glass surfaces were freshly cleaned in persulfuric acid for 2 h and then rinsed thoroughly with water and dried in vacuum overnight before silylation. The hydrophobized glass surfaces were prepared by the silylation process described above.

METHODS

Measurement of Adsorption by OWLS

For monitoring the polymer adsorption at the solid–liquid interface an OWLS 110-type instrument (MicroVacuum, Budapest, Hungary) controlled by a personal computer was used. OWLS is an optical sensor technique using an electromagnetic evanescent field for sensing surface processes at the molecular level. The OWLS technique is based on the measurement of the incoupling angle of a linearly polarized laser beam (He-Ne laser, 632.8 nm) diffracted on a fine optical grating in a thin optical waveguide layer. Such incoupling resonance occurs at very precise angles of incidence, depending on the complex refractive index of the optical sensor and the sample medium. The refractive index, determined from the incoupling angle, allows *in situ*, continuous, label-free determination of layer thickness and coverage (or mass) of the adsorbed or bound material with ultrahigh sensitivity. The detection limit of the technique is a few pgmm^{-2}. More details on the method and on the physical principles can be found at www.microvacumm.com. The experimental setup was equipped with a flowthrough cuvette (0.01 ml) to introduce the liquid sample solution to the grating part of the sensor surface in a reproducible manner.

Prior to the start of the adsorption measurements, the surface was allowed to stabilize underwater for at least 24 h. In the base-line run, when the stabilized sensor surface was in contact with water the refractive index, n_F, and the thickness of the waveguiding film, d_F, were determined. In the adsorption experiment Pluronic solution with a selected concentration was introduced into the sample chamber mounted onto the sensor surface. The progress of the adsorption, indicated by the change in two characteristic parameters, the refractive index in the vicinity of the solid surface, n_A, and the adsorption layer thickness, d_A, was followed simultaneously. After equilibration (which took less than a few minutes in our case) 2 ml of the solution with a higher concentration was introduced, and the same procedure was repeated up to the Pluronic concentration of $10\,\mathrm{gdm}^{-3}$. The adsorbed amount of the Pluronic on the sensor surface, m_A, can be directly calculated from the thickness and refractive index values according to the Feijter formula [30].

$$m_A = d_A(n_A - n_C)(dn/dc)^{-1}, \tag{1}$$

where d_A is the adsorption layer thickness, n_C is the refractive index of the solution, and dn/dc is the refractive index increment of the adsorbed material. For Pluronics, a refractive index increment value of 0.132 cm^3g^{-1} was used [31] for the calculations, and the adsorbed amount could be determined with an accuracy of $\pm 2\,ngcm^{-2}$. Standard deviations displayed on the adsorption isotherms are due to differences between parallel measurements.

Wettability Measurements

Wettability of solid surfaces by water and aqueous Pluronic solutions in a concentration range of $10^{-3}-1$ gdm^{-3} were studied tensiometrically. Wetting force, F_w, was measured by a force transducer, with the accuracy of $\pm 10^{-6}$ N connected to a personal computer while immersing the solid sample as a Wilhelmy-plate into the liquid and withdrawing it at a constant speed of 1 cm/min. The wetting tension, $\tau = \gamma \cos \Theta$, due to the capillary rise at the vertical plate can be determined from the measured force extrapolating to zero and to the maximum immersion,

$$F_w = p\gamma \cos \Theta, \tag{2}$$

where p is the length of the three-phase contact line, γ is the surface tension of liquid, and Θ is the advancing or receding contact angle. Knowing the surface tension of the liquid, the advancing and receding contact angles, Θ_A and Θ_R, can be obtained from the immersion and emersion sections of the force curve; details are described elsewhere [32–34]. The sensitivity of the force sensor allows us to calculate the contact angle with an accuracy of 0.1° in the low and 0.01° in the high contact angle range. However, the standard deviation of contact angles, typically ±2°, represents the reproducibility of sample preparation. At least three measurements with three solid samples were carried out for each system. The wetting effect of Pluronic solutions was investigated by performing two immersion cycles. Between the immersions a 10 min soaking time in the Pluronic solution [15] was introduced to allow the adsorption of Pluronic onto the solid surface.

RESULTS AND DISCUSSION

Adsorption Measured by OWLS

Adsorption isotherms of the four selected Pluronics are shown in Figure 1. The substrate was the silylated OWLS sensor with a hydrophobic surface characterized by advancing water contact angle of $75 \pm 3°$. As can be seen, the highest adsorbed amount was measured for PE10300 on the sensor surface with a sharp increase at low concentration of this Pluronic in a narrow range. Pluronic 10300 is the most

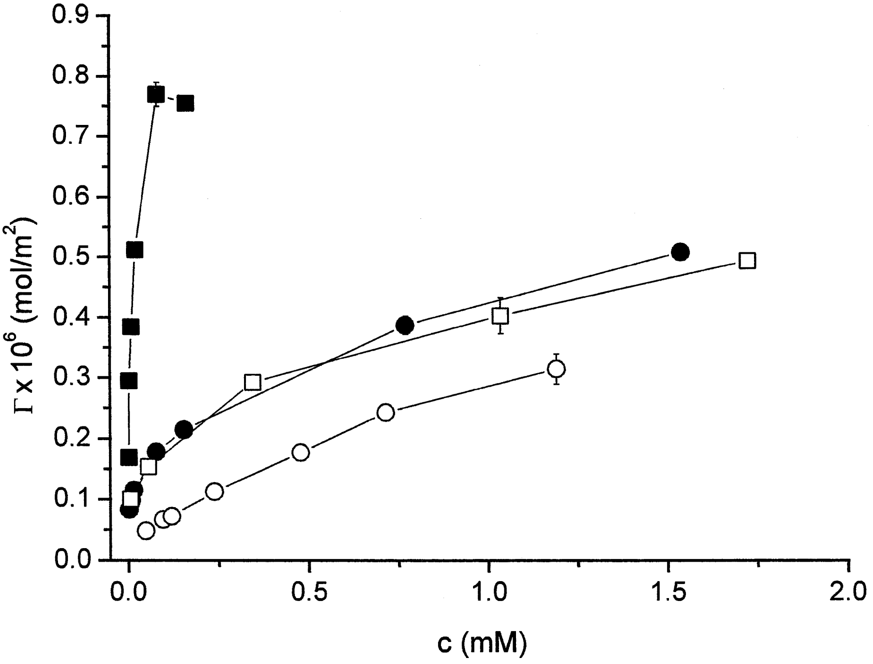

FIGURE 1 Adsorbed amount of Pluronic on hydrophobized OWLS sensor surface as a function of Pluronic PE10300 (■), PE10500 (●), PE6400 (□), and PE6800 (○) concentration.

hydrophobic compound used in this study, and its low solubility in water terminates the isotherm. The adsorbed amount for the three other Pluronics applied here increases gradually with the concentration. Both PE10500 and PE6400 display higher amounts of surface excess than the PE6800, which is the most hydrophilic polymer among the selected ones. Neither the plateau region nor the sudden increase in the adsorbed amount just before the critical micellar concentration, c_M [15], of the surfactant were reached in our experiments. The progressive increase of the adsorbed surfactants of PE6400 and PE6800 with the concentration is not expected since the concentration range applied here is far below their c_M values (see Table 1). The similar increase of adsorption of PE10500 is somewhat ambiguous when we consider only the c_M of that Pluronic.

The adsorbed amount of Pluronics on this hydrophobic surface clearly correlates to their HLB values, indicating that the driving force for the adsorption seems to be the combined effect of the capability of the PPO segment to adsorb at the interface and the polarity, poor solubility of the whole molecule, or both. The PE10300 and PE10500 contain the same hydrophobic central PPO blocks but show quite different adsorption due to their various polarities arising from 30 and 50% PEO contents, respectively. However, the PE10500 and PE6400 characterized by the same HLB values but different compositions resulted in similar adsorption behavior.

The adsorbed amounts obtained for the highest bulk concentrations applied (10 $\mathrm{g\,dm^{-3}}$, except for PE10300, where 1 $\mathrm{g\,dm^{-3}}$ due to the lower solubility) are presented in Table 1 together with the measured layer thicknesses and calculated molecular areas. The differences among the layer thicknesses of the four Pluronics are somewhat less than one would expect from the very different PEO chain length, which means that the conformation status of the chains might be different for the various Pluronics. One could speculate that the layer thickness values might be close to the highly extended PEO chain length for the PE10300 and PE6400 with the shorter PEO segments. In the cases of longer PEO blocks the layer thickness values hardly exceeding the double radius of gyration denote more coiled hydrophilic segments in the adsorbed layer.

The areas occupied by one molecule are close to the values reported earlier for PE10500, *i.e.*, 4.0 $\mathrm{nm^2}$ [13], and for PE6800, *i.e.*, 8.7 $\mathrm{nm^2}$ [9], and roughly follow the order of molecular weight of the Pluronics. These adsorption results indicated that the order of the adsorption ability of the Pluronics examined in the present study on a hydrophobic solid surface is PE10300 $>>$ PE10500 $\sim$ PE6400 $>$ PE6800.

Wettability Studies

Wetting tension measured by the Wilhelmy-plate technique represents the combined effect of surface tension of the liquid and wettability of the solid surface. Wetting tension values obtained for PLGA70/30 surfaces in various Pluronic solutions of different concentrations are displayed in Figure 2. At the first immersion of the polymer surface into the given solutions (Figure 2a) no significant effect can be observed among the Pluronic solutions and their concentrations compared with the wetting tension of water (when taking into account the average value of standard deviation of surface reproducibility as $\pm 2\,\mathrm{m\,N\,m^{-1}}$). After the second immersion following an adsorption period of 10 min, the wetting tension is higher than that of water and increases with the concentration (see Figure 2b). The comparison of the various Pluronics reveals (Figure 2b) that PE10300 and PE10500 seem to be the most powerful ones in improving the

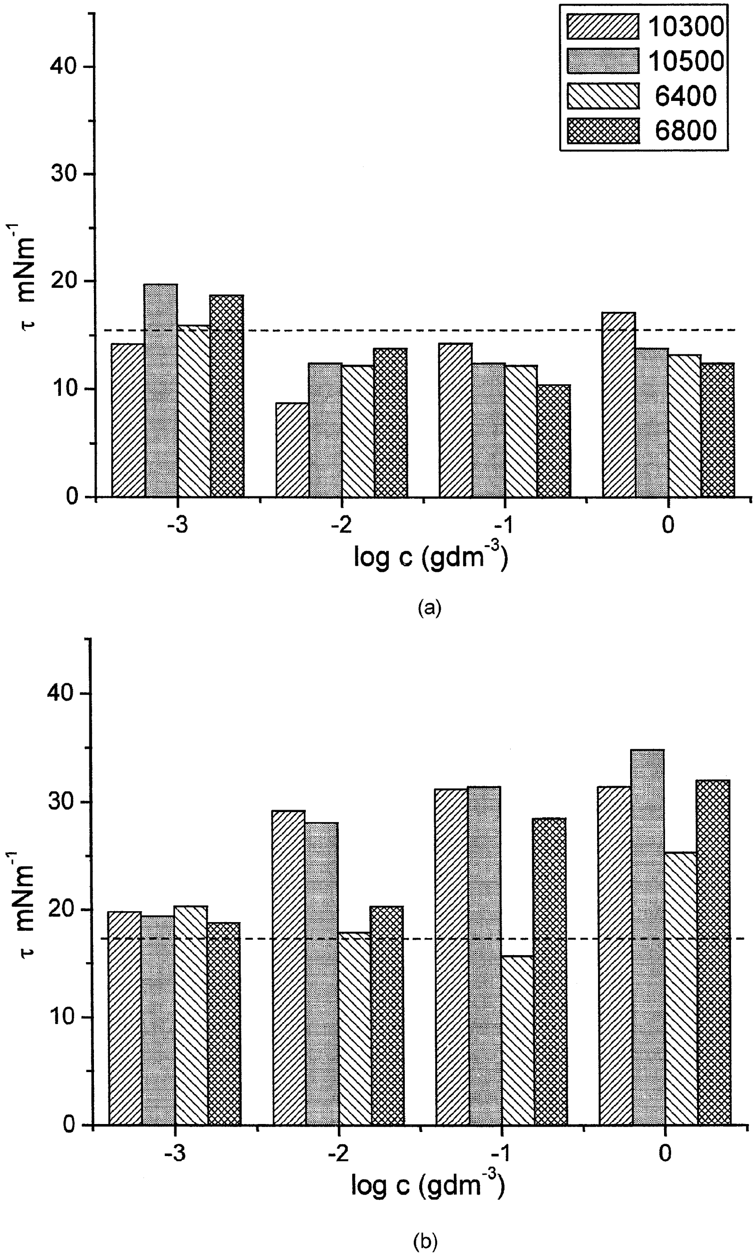

FIGURE 2 Wetting tension, $\tau = \gamma \cos\Theta$, of PLGA70/30 surfaces in Pluronic solutions at concentrations of 10^{-3}, 10^{-2}, 10^{-1}, and 1 gdm^{-3}: (a) first immersion and (b) second immersion following 10 min adsorption. The wetting tension of the PLGA70/30 surface in water is displayed with a dashed line for comparison.

wettability, while PE6800 also has a similar effect at the two highest concentrations. The difference between the results of the first and second immersions (Figures 2a and 2b) demonstrates that the adsorption of Pluronics with different structure and HLB values onto the hydrophobic surfaces has a specific role in the alteration of wettability and that this process takes some minutes, as was shown in detailed kinetic studies [15, 35].

Based on the above results, the wetting effect of the different Pluronic compounds, $\Delta\Theta_A^*$, is defined as the difference of contact angle of water and the contact angle of Pluronic solution on the solid surface measured in the second immersion cycle. It has to be kept in mind while evaluating the results, that the advancing contact angles calculated from the wetting tension measured during the second immersion into the Pluronic solutions are not true contact angles of the liquid on a solid surface but rather apparent angles (Θ_A^*) of the solution on the solid modified by the Pluronic adsorption. In the pharmaceutical application of Pluronics, however, this is the real condition, because the solid hydrophobic drug carrier has to be made more hydrophilic by surfactant adsorption. These $\Delta\Theta_A^*$ data are plotted for PLGA70/30 as well as for another hydrophobic surface, silylated glass, for

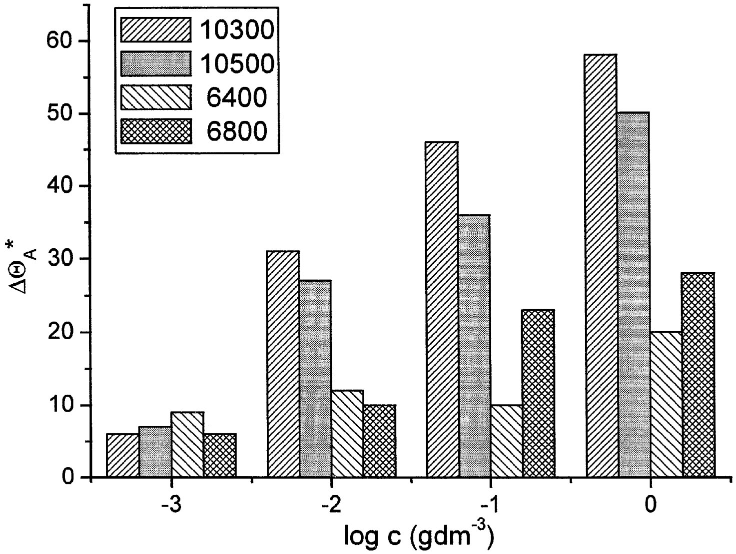

FIGURE 3 Wetting effect, $\Delta\Theta_A^*$, as the difference between the advancing contact angles of water and that of Pluronic solutions measured at the second immersion of the PLGA70/30 surfaces at Pluronic concentrations of 10^{-3}, 10^{-2}, 10^{-1}, and 1 gdm^{-3}.

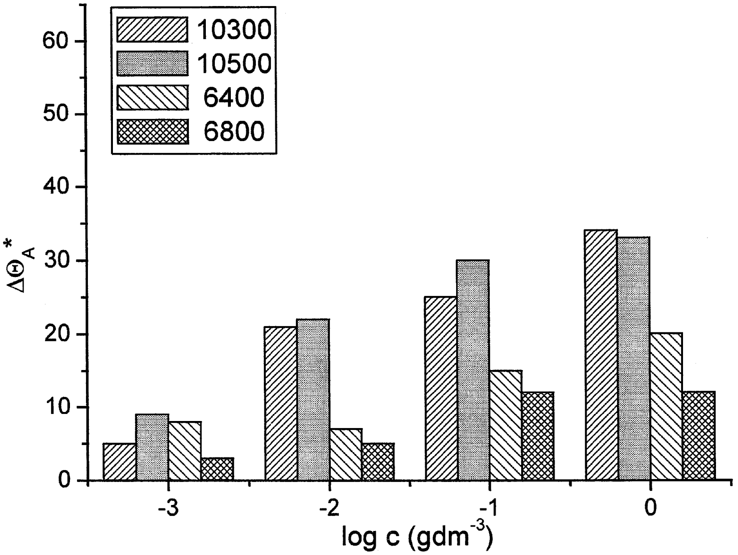

FIGURE 4 Wetting effect, $\Delta\Theta_A{}^*$, as the difference between the advancing contact angles of water and that of Pluronic solutions measured at the second immersion of the hydrophobized glass surfaces at Pluronic concentrations of 10^{-3}, 10^{-2}, 10^{-1}, and $1\,\mathrm{gdm}^{-3}$.

comparison in Figures 3 and 4, respectively. A considerable wetting effect can be observed on both surfaces from the Pluronic concentration of $10^{-2}\,\mathrm{gdm}^{-3}$. The change in the contact angle on the PLGA70/30 surface can reach 50 degrees with increasing concentration for the most effective surfactants, PE10300 and PE10500. The wetting effect on the hydrophobized glass surface shows a similar pattern but much lower values. This deviation can be attributed to the difference in the wettability (or polarity) of the two hydrophobic surfaces. The PLGA70/30 copolymer surface before Pluronic adsorption is characterized by advancing and receding water contact angles of $\Theta_A = 77.0 \pm 0.6$ and $\Theta_R = 54.3 \pm 0.8$, respectively, while the corresponding values for the hydrophobized glass surface are $\Theta_A = 96.5 \pm 2.3$ and $\Theta_R = 68.0 \pm 4.0$. The surface energies of such surfaces are calculated from the advancing water contact angles as 36.6 ± 0.4 and $24.6 \pm 1.4\,\mathrm{mNm}^{-1}$, respectively, according to the Neumann equation [36, 37]. That lower surface energy of the hydrophobized glass surface might be the reason for the observation that the decrease in contact angle caused by Pluronic solutions is smaller than for the chemically inhomogeneous copolymer, PLGA70/30, due to a different adsorption of the Pluronic on the silylated glass surface (it could not be measured by the technique applied). For the copolymer PLGA70/30 the wettability, hence $\Delta\Theta_A^*$, increases in the following order: PE6400 < PE6800 < PE10500 < PE10300. The same order for the hydrophobic glass surface is: PE6800 < PE6400 < PE10500 < PE10300, which corresponds to the order of the increasing adsorption measured for the silylated sensor surface by the OWLS method.

It might be expected that the hydrophilic PEO blocks of the adsorbed Pluronic molecules are responsible for the change of wettability of the surface, namely the decrease in the contact angle. The wetting effect as a function of the adsorbed amount of PEO considering the various Pluronics is presented in Figure 5. There is a clear tendency indicating that the higher surface concentration of PEO results in greater improvement of the wettability, independently of the type of Pluronic molecule. The means by which this high PEO concentration in the adsorbed layer can be reached is very much dependent on the adsorption behavior of the given Pluronics. The comparison of the adsorption and wettability results can lead to the conclusion that

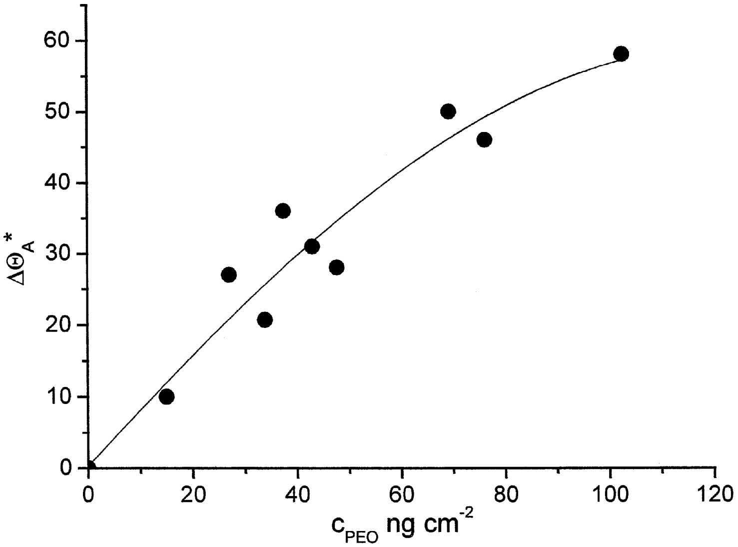

FIGURE 5 Wetting effect, $\Delta\Theta_A^*$, as the difference between the advancing contact angles of water and that of Pluronic solutions measured at the second immersion of the PLGA70/30 surfaces as a function of adsorbed amount of poly(ethylene oxide).

the Pluronic with the highest PEO content is not necessarily the best candidate for wetting purposes. Contrary to that, when solutions with the same concentrations are compared, the PE10300 proved be the most effective, even if its PEO content was the lowest among the four selected Pluronics. Although more studies should be done on different polymeric drug carriers in the future, it can be still safely stated that the selection of the most potent wetting agent for surface modification can be predicted by comparing adsorption data of the Pluronics and their wettability data measured on the given polymeric surfaces.

CONCLUSIONS

Adsorption behavior of four surface-active block copolymers, Pluronics with various compositions, on hydrophobic surfaces was compared with their efficacy as wetting agents. The molar adsorbed amount of Pluronics clearly correlates to their hydrophobic property characterized by the HLB value. The wetting effect of aqueous Pluronic solutions is closely related to their adsorption at the solid–liquid interface. A considerable decrease in the apparent advancing contact angle was achieved at the interface, modified by the adsorption of the most effective Pluronics, PE10300 and PE10500, at 10^{-2} gdm^{-3} or higher concentrations. The relationship between the adsorption properties and wetting effect of these PEO-containing compounds can provide a valuable tool in design of surface modification of hydrophobic drug carriers.

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