Volumes 123–126, November 16 2006
Completing volumes 123–126

ISSN: 0001-8686

ELSEVIER

Advances in
COLLOID and INTERFACE SCIENCE

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ELSEVIER
Advances in Colloid and Interface Science 123–126 (2006) 345 – 351
ADVANCES IN COLLOID AND INTERFACE SCIENCE
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Dynamics of micelles of the triblock copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) in aqueous solution

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Abstract

A number of results reported on the kinetics of exchange of triblock copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), PEO–PPO–PEO, between micelles and the intermicellar aqueous solution are reviewed and analyzed to extract the rate constants k^+ for the entry of a copolymer into a micelle and k^- for the exit of a copolymer from a micelle. Contrary to what is generally observed for conventional surfactants, the rate constant for the entry of a copolymer into a micelle is slower to much slower than for a diffusion-controlled process and decreases as the degree of polymerization of the PO block, n_{PO}, increases. The effect of the degree of polymerization of the EO block, n_{EO}, on the two rate constants is significant only for low values of n_{EO}. The variation of k^- with n_{PO} strongly suggests that the free copolymer molecule adopts a conformation where the PO block is tightly coiled with little contact with water and not a fully extended and hydrated conformation, in contrast to what is commonly assumed when analyzing the dependence of the cmc on the polymerization degree of the hydrophobic block.

Contents

1. Introduction

Amphiphilic block copolymers have been extensively investigated in view of their many applications [1]. In aqueous solutions these copolymers give rise to micelles at concentrations C above the critical micellization concentration, cmc. Similarly to surfactant micelles, amphiphilic block copolymer micelles are not frozen objects, at least when the copolymer molecular weight is relatively low. The two main spontaneous dynamic processes that occur in micellar solutions of surfactants, i.e., the exchange of surfactants between micelles and bulk phase and the micelle formation/breakdown, also occur in micellar solutions of amphiphilic block copolymers. In the case of micellar solutions of conventional surfactants, whether ionic, nonionic or zwitterionic, it has been consistently found that the entry of a surfactant into its micelles is nearly controlled by diffusion, with values of the entry rate constant k^+ in the 10^8–10^9 M^{-1} s^{-1} range for surfactants with an alkyl chain containing up to 14 to 18 carbon atoms, depending on the surfactant [2,3]. The value of k^+ decreases very slowly upon increasing surfactant chain length. On the contrary, the rate constant k^- for the exit of a surfactant from its micelles decreases exponentially when the carbon number m of the surfactant alkyl chain is increased, by a factor close to 3 per additional methylene group [2,3]. This factor corresponds to an increment of about 1.1kT per methylene group in the free energy of transfer of a surfactant from a micelle to the aqueous phase. Micelles of conventional surfactants form and breakdown either by a series of reactions of entry/exit of a single surfactant at a time into/from micelles [4] or by reactions of fusion/fission (also

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doi:10.1016/j.cis.2006.05.011

referred to as fragmentation/coagulation) involving submicellar aggregates [5], depending on the experimental conditions (nature and concentration of the surfactant; ionic strength; additives; temperature; etc.). These results also hold for dimeric (gemini) surfactants with a short alkyl chain (say 8 carbon atoms) [6]. However, gemini surfactants with a longer alkyl chain (12 carbon atoms) depart from this scheme and the entry rate constant was found to be up to 100-fold slower than for a diffusion-controlled process [7].

The dynamics of amphiphilic block copolymer micelles in aqueous solution has been investigated both experimentally [8,9] and theoretically [10–12] with the view to understand the mechanism by which block copolymer micelles form and break down and also for determining the rate constants for the copolymer exchange between micelles and bulk phase. It has been found that these processes are more complex and also much slower than with surfactants [8,9]. Actually, in most instances, the processes are so slow as to be referred to as ‘frozen’, with the systems taking days, months or even longer times to reach equilibrium, after being submitted to a perturbation that affects micelles [8,9].

One series of amphiphilic copolymers, the triblock poly (ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), PEO–PPO–PEO (EO = ethylene oxide; PO = propylene oxide), show a relatively fast relaxation behavior that permits its study by means of chemical relaxation methods. These copolymers are not the simplest ones from the structural viewpoint. Nevertheless they have been much investigated essentially because they are commercially available with a wide range of composition and molecular weight [1,13,14]. In aqueous solution they give rise to micelles with a core mainly made up of PO chains and a corona made up of EO chains and water at temperatures above the so-called critical micellization temperature, cmT [13,14] (the value of the cmc of a copolymer solution of concentration *C* is close to *C* at a temperature equal to the cmT). The cmc of PEO–PPO–PEO aqueous solutions decreases very rapidly as the temperature is increased [13,14]. The relaxation processes observed with micellar solutions of PEO–PPO–PEO copolymers have been assigned with reasonable certainty to micellar equilibria [15–25]. The relaxation behavior of these systems is similar to that of surfactant solutions, with two well separated relaxation processes that have been mainly investigated by the temperature-jump (T-jump) technique, with Joule effect or laser heating. The time dependence of the intensity of light scattered by the copolymer solution after rapidly raising the solution temperature has been used to monitor the relaxation [16–18,20,22–24]. The slower of the two relaxation processes has been assigned to the micelle formation/breakdown. The concentration dependence of the associated relaxation time suggested that this process mainly occurred via fusion/fission of submicellar aggregates [16,20–22]. This process can be quite slow and it is not always observed. It is not further considered in this paper. The faster relaxation has been attributed to the copolymer exchange between micelles and bulk phase [15–25]. It occurs in a convenient time-scale and data have been reported for PEO–PPO–PEO copolymers of varied composition and molecular weight. Hecht and Hoffmann reported the first investigation of the relaxation behavior of PEO–PPO–PEO copolymers [15]. They observed a single relaxation process which they attributed to the copolymer exchange and reported values of the entry rate constant in a micelle about 100 times slower than for a diffusion-controlled process. Since this pioneering study kinetic data have become available for more PEO–PPO–PEO copolymers [16,18,20,25].

The primary purpose of starting this work was to analyze the available kinetic data for PEO–PPO–PEO solutions in order to extract values of the rate constants k^+ and k^- and see their trends when the degree of polymerization of the EO and PO blocks varied. As a second step, we wanted to analyze these data in order to obtain information on the conformation of the free (non-micellar) block copolymer in water. Indeed two widely differing models are present in the literature: one where the hydrophobic block is coiled but contacts between water and hydrophobic units are permitted [26] and another where the hydrophobic block forms a globule that permits water/hydrophobic unit contacts only at the surface of the globule [10,12]. A first attempt to achieve these goals unfortunately used incorrect values for some of extracted rate constants [9].

As is shown below the determination of reliable values of the rate constants is difficult owing to the lack of data, mainly of values of the micelle aggregation number. Another difficulty arises because the k^+ and k^- values are not all obtained at the same temperature and must, therefore, be corrected for temperature on the basis of available theories for polymer solutions. Nevertheless, the set of k^+ and k^- values reported below permitted us to reach some valuable conclusions. Most notably, *both* k^- and k^+ are found to decrease as the degree of polymerization n_{PO} of the PO block increases. The entry of a copolymer in a micelle is close to being diffusion-controlled for copolymers with a short hydrophobic block but becomes much slower as n_{PO} is increased. The effect of the degree of polymerization n_{EO} of the EO block on the two rate constants is much weaker. The variations of the rate constants with n_{PO} support a model of the free (non-micellar) copolymer where the hydrophobic block is strongly coiled, forming a globule, with little contact with water.

2. Evaluation of the rate constants for the exchange of PEO–PPO–PEO copolymers between micelles and bulk phase

Table 1 lists the copolymers for which kinetic data have been reported for the exchange process and their characteristics: molecular weight, M_{w}, PO weight percent and cmc value at the temperature at which the kinetic data are reported. The values of the rate constants k^+ and k^- for the entry/exit of a copolymer in/from its micelles have been extracted from the reported data as follows on the basis of Eqs. (1) and (2):

$$1/\tau_1 = (k^-/N)(N/\sigma^2 + C_{\mathrm{red}}) \qquad (1)$$

and

$$k^- \approx k^+/\mathrm{cmc} \qquad (2)$$

In Eq. (1), τ_1 is the relaxation time measured for the exchange process, σ is the mean standard deviation of the distribution of

Table 1
Characteristics of the PEO–PPO–PEO block copolymers and values of the exchange rate constants

Copolymer [a]		M_w (g mol^{-1}) [a]	PO [b] (wt.%)	T [a] (°C)	cmc [a] (mM)	N	k^+ (M^{-1} s^{-1})	k^- (s^{-1})	Reference
L64	$EO_{13}PO_{30}EO_{13}$	2920	60	40	0.9 [c]	40 [c]	2.4×10^8	2×10^5	[25]
F88	$EO_{103}PO_{39}EO_{103}$	11 400	20	40	0.55	40	2×10^7	1.1×10^4	[15]
P85	$EO_{26}PO_{40}EO_{26}$	4600	50	37.7	0.21	40 [d]	4×10^8	8.4×10^4	[18]
P84	$EO_{19}PO_{43}EO_{19}$	4200	60	27	3.6	40	1.8×10^7	6.7×10^4	[20]
F108	$EO_{132}PO_{50}EO_{132}$	14 600	20	32	0.28	40	4.9×10^6	1.4×10^3	[18]
P104	$EO_{27}PO_{61}EO_{27}$	5900	60	24.2	0.65	50 [e]	5.9×10^6	3.8×10^3	[18]
F127	$EO_{100}PO_{65}EO_{100}$	12 600	30	21.1	2.2	35 [f]	1.7×10^6	3.8×10^3	[15]
P123	$EO_{19}PO_{69}EO_{19}$	5750	70	21.4	0.14	40	10×10^6	1.5×10^3	[15]

[a] From Alexandridis et al. [13], unless indicated otherwise.
[b] From Alexandridis and Hatton [14].
[c] From Thurn et al. [25].
[d] From Almgren et al. [29].
[e] From Nivaggioli et al. [27].
[f] From Nivaggioli et al. [27].

micelle aggregation number assumed to be a Gaussian distribution, N is the average micelle aggregation number and $C_{red}=(C-\text{cmc})/\text{cmc}$ is the reduced surfactant concentration. The combination of Eqs. (1) and (2) results in

$$1/\tau_1 = (k^+/N)(C-\text{cmc}) + k^-/\sigma^2 \tag{3}$$

Eq. (3) has been used to analyze variations of $1/\tau_1$ with C whenever available.

P123 and F88: Hecht and Hoffmann [15] report the variation of $1/\tau_1$ with C for these two copolymers. These data have been analyzed by drawing straight lines through the data points at low C, discarding the results at high concentration where significant changes of micelle size can occur and affect the variation of $1/\tau_1$ with C. The slope of the plots is equal to k^+/N (see Eq. (3)). Values of N for these two copolymers are not reported. Hecht and Hoffman [15] used the value $N=25$ but several reports [25,27–31] suggest that the value $N=40$ is probably closer to the real value. The resulting values of k^+ and k^- are listed in Table 1.

F127: The $1/\tau_1$ vs. C plot for the F127 copolymer reported in Hecht and Hoffmann [15] is highly nonlinear. The rate constant k^+ was evaluated from the slope of the plot drawn through the data points at $C=2.7$ and 5 wt.% (2.2 and 4 mM), using a cmc value of 2.2 mM at the temperature of 21.1 °C at which the experiments were performed [13,14], and $N=35$ [28].

P85: Goldmints et al. [18] reported a series of plots of τ_1 vs. $T-\text{cmT}$ for various concentrations of this copolymer. From these data a plot of $1/\tau_1$ vs. C at 37.5 °C was prepared and analyzed using Eqs. (1)–(3) and the reported value of N [29] to yield the listed values of k^- and k^+.

P84: The numbers on the $1/\tau_1$ axis of Fig. 5 in Waton et al. [20] are incorrect and should read 10^3 and 10^4 instead of 10^4 and 10^5 [32]. The value of $1/\tau_1$ at 27 °C was used to obtain that of k^-, using Eq. (1), with $N=40$ and assuming that $\sigma^2/N=1$. This last assumption rests on the extensive results available for conventional surfactants [2,3]. For copolymers the distribution is expected to be even narrower. The same assumption was also made for the copolymers P104 and F108 below.

P104 and F108: The reported τ_1 vs. $T-\text{cmT}$ data at a given C (see Fig. 4 in Goldmints et al. [18]) for these two copolymers have been used to obtain the k^- values as follows. A generally low value of $T-\text{cmT}$ was selected and the corresponding value of τ_1 was obtained from the plot at the given C. The values of the cmT for the solution of concentration C and of the cmc for the investigated copolymer at temperature T were obtained from the available cmT vs. C data [13,14]. The value of N has been reported for P104 [27] but not for F108 for which it was taken equal to 40. The rate constants were then obtained using Eqs. (1) and (2).

L64: The values of the rate constants for this copolymer are those from Thurn et al. [25]. They have been obtained from the $1/\tau_1$ vs. C plot, using Eqs. (1) and (2) and the values of the cmc and N listed in Table 1.

The values of the rate constants k^- and k^+ are listed in Table 1 in the order of increasing value of the degree of polymerization of the PO block. It is realized that the errors in the listed values are large and that the different values correspond to temperatures ranging between 21 and 40 °C. Nevertheless, the overall variations are quite large, with the values of both k^- and k^+ stretching over slightly more than two orders of magnitude. The values of k^+ are all between 2.4×10^8 and 1.7×10^6 M^{-1} s^{-1}, that is smaller to much smaller than for a diffusion-controlled process ($k_{diff}\approx 10^9$ M^{-1} s^{-1}). Thus the present k^+ data confirm and extend the finding of Hecht and Hoffmann [15], namely that the entry of a copolymer in its micelles is slower than for a diffusion-controlled process. Once a free copolymer has collided with a micelle some process must take place before its is successfully incorporated into the micelle. This process may be a slow penetration of the hydrophobic block through the hydrophilic corona. It probably also involves a conformation change of the hydrophobic block.

Figs. 1 and 2 show the variation of k^- and k^+ with the degree of polymerization n_{PO} and n_{EO} of the hydrophobic and hydrophilic blocks, respectively, using a semi-logarithmic representation. The variations of the rate constants with n_{PO} are roughly linear and fairly significant (see Figs. 1A and 2A). The variations with n_{EO}

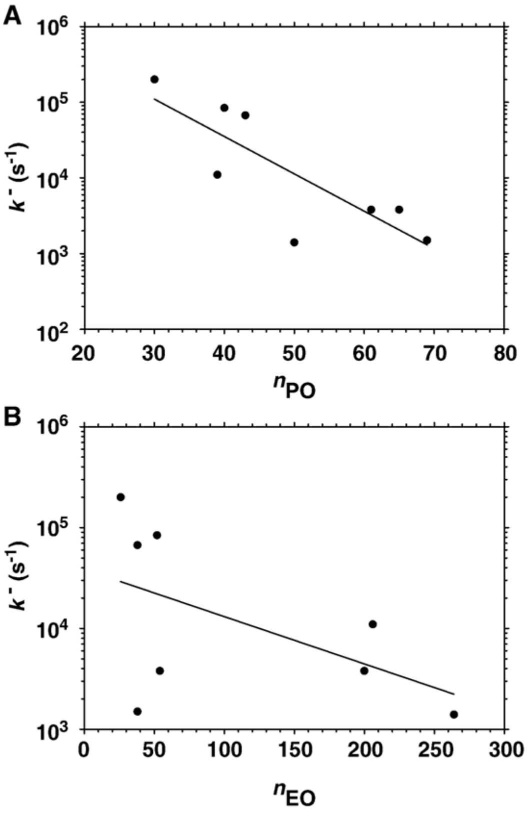

Fig. 1. Variation of the exit rate constant k^- with: (A) the degree of polymerization of the propylene oxide block, n_{PO}; and (B) the degree of polymerization of the ethylene oxide block, n_{EO}.

(Figs. 2A and B) are much less important. For conventional surfactants the plots k^- vs. m (surfactant alkyl chain carbon number) have been used to extract the free energy increment for the transfer of a methylene group of the alkyl chain from the micelles to the aqueous phase [2,3]. This is possible because the free energy of transfer of a surfactant from a micelle to water varies linearly with m [33]. The plots in Fig. 1A and B could be similarly used to obtain the free energy increments for the transfer of a propylene oxide unit and of an ethylene oxide unit from the copolymer micelles to the aqueous phase, if one assumes that the free copolymer adopts a conformation where the EO block and more particularly the PO block are in full contact with water. Both blocks can be coiled but with very few contacts between PO units (or EO units). In such a model the free energy of transfer of a copolymer would vary nearly linearly with both n_{PO} and n_{EO}. The slope of the plots in Fig. 1 yield the values of the free energy of transfer from the micelles to the aqueous phase $\Delta G^\circ_{tr}(PO) = 0.11kT$ and $\Delta G^\circ_{tr}(EO) = 0.01kT$. The value of $\Delta G^\circ_{tr}(PO)$ is small and still represents an upper bound. Indeed, in Fig. 1A, the data points for the low n_{PO} values generally correspond to higher temperature than the points for larger n_{PO} values. Thus, a correction to the data for temperature will result in a decrease of the slope of the plot and in a value of the energy of transfer still lower than $0.11kT$.

This value of $\Delta G^\circ_{tr}(PO)$ is unrealistically low. This is realized when comparing it to the value $0.25kT$, obtained from the plot of log cmc vs. n_{PO} [31]. This last value itself is quite low and suspicious. Indeed the free energy of transfer of a propylene group is about three-fold that of a methylene group, i.e., $3.3kT$. The addition of an ether oxygen to a propylene group, thereby making up a propylene oxide unit, is expected to decrease this value to some extent but certainly not by $3kT$ [34]. We are thus led to discard the possibility that the PO block adopts a fully hydrated conformation in the free (non-micellar) PEO–PPO–PEO copolymer in aqueous solution. The PO block probably takes on a tightly coiled conformation favoring contacts between the hydrophobic PO units. This is actually the current view of the structure of amphiphilic block copolymers. It is also adopted in theories dealing with the exit of a copolymer from its micelles [10–12]. As the hydrophobic (solvophobic) block comes into contact with the solvent it coils over itself favoring contacts between the hydrophobic repeat units and avoiding contacts between these units and the solvent. This leads to a more complex dependence of log k^- on n_{PO}. Below we use a current theory of copolymers to obtain an analytical form of the dependence of log k^- on n_{PO} that also permits us to correct for the effect of temperature.

3. Theory for the analysis of the dependence of the exit rate constant on the polymerization degree of the hydrophobic block

The treatment that follows is based on the available data from a scaling analysis of micelle formation by amphiphilic

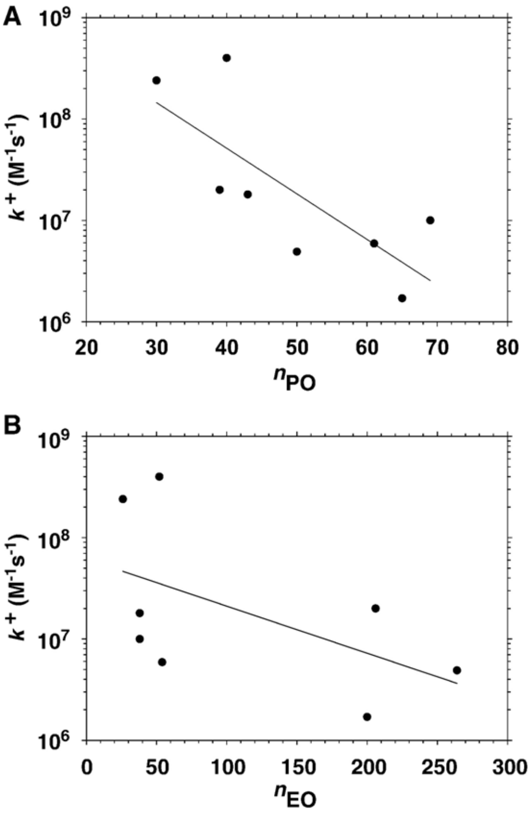

Fig. 2. Variation of the entry rate constant k^+ with: (A) the degree of polymerization of the propylene oxide block, n_{PO}; and (B) the degree of polymerization of the ethylene oxide block, n_{EO}.

block copolymers. At this level of approximation the equilibrium structure of triblock copolymer micelles is identical to the structure of diblock copolymer micelles that would be obtained by cutting the hydrophobic blocks at their middle. Our analysis follows standard models [10,35,36] for diblock copolymer micelles comprising N copolymer chains, each with polymerization degrees n_p and n_h, where subscripts 'p' and 'h' stand for polar and hydrophobic repeat units. From this point on, n_{EO} and n_{PO} are substituted for n_p and n_h but it must be kept in mind that the analysis below also applies to other block copolymers in solvents other than water.

Three different types of micelles are to be distinguished according to the relative molecular weights of the polar (soluble) and hydrophobic (insoluble) blocks. When the soluble block is very large the solvated corona is much larger than the dense core, a geometry usually referred to as the star-like micelle. In this region of parameter space the micelle size is limited by the excluded volume interaction and the preferred aggregation number N grows with hydrophobic block length as $n_{PO}{}^{4/5}$ [10]. For small hydrophilic block lengths the corona thickness is much smaller than the core radius, a geometry known as large-core or "crew-cut" micelles [10]. In this regime, the micelle size is limited by the stretching of the chains making up the hydrophobic core and the preferred aggregation number N grows as n_{PO} [10]. It is important to stress that in both of these main regimes the aggregation number depends mainly on the length of the hydrophobic block. For intermediate asymmetries, in the range $n_{PO}{}^{11/18} < n_{EO} < n_{PO}{}^{11/15}$, the size of the corona is of the order of, or smaller than the core radius, but the micelle size is still controlled by excluded volume interactions in the corona [35]. This small intermediate regime merely provides a smooth crossover between the two main regions in parameter space and will not be mentioned further. Two more equilibrium quantities may be of interest: the chemical potential at coexistence $\mu \approx n_{PO}{}^{2/3}/N^{1/3}$, and the width of the micelle size distribution around its preferred value $\delta N \approx N^{2/3}/n_{PO}{}^{1/3}$, which is not very sensitive to the hydrophobic block length [35]. Note that even in the large-core regime, the polar blocks typically build up an excluded volume barrier against unimer (free copolymer) penetration.

In an aqueous copolymer solution, any exchange kinetic mechanism that does not preserve the number of copolymer micelles in the solution is usually very slow (process of micelle formation/breakdown, see above) and equilibrium estimates for the kinetic constants are in general irrelevant partially because values for the cmc of these macromolecular surfactants are below the detection threshold of available techniques [8,9]. In the experiments under consideration for the PEO–PPO–PEO block copolymers the chains in the core are only moderately hydrophobic and values for the cmc are within reasonable limits, in the 0.1–10 mM range. It seems therefore reasonable to base the estimate of the copolymer residence time in micelles, T_R, on equilibrium estimations of the relevant quantities. The expulsion of a unimer from a micelle is an activated process. The main contribution to the activation energy, W, comes from the surface tension of the collapsed hydrophobic block into a globule as it exits the micelle [10,12,36] and is given in thermal units by:

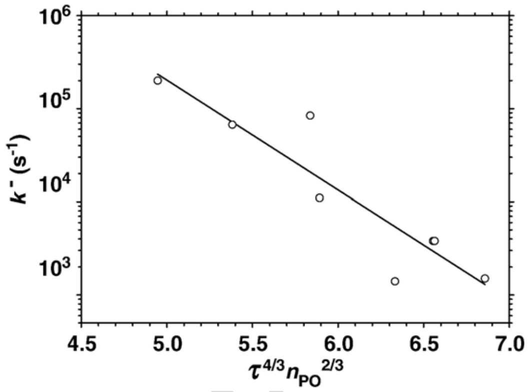

Fig. 3. Variation of the exit rate constant k^- with the quantity $\tau^{4/3} n_{PO}{}^{2/3}$. The straight line going through the data points represents the best fit of the data.

$$W = 4\pi\gamma R^2 = \gamma(6\pi^{1/2} n_{EO}/\rho)^{2/3} \tag{4}$$

In Eq. (4), γ is the surface tension of the globule/water interface, R is the radius of the globule and ρ is the number density of hydrophobic monomers in this globule. Note that this contribution is independent of diblock copolymer asymmetry. Other asymmetry-dependent contributions such as the variation of configuration entropy of the hydrophobic block ($\propto n_{PO}{}^{1/3}$) upon expulsion caused by compression in the collapsed globule or stretching in the large-core micelle, or the repulsion by the corona ($\propto N^{1/2}$), are less important and will be neglected. Once a globule is formed outside the core, it is driven out of the corona region by the osmotic pressure gradient, and it will not come back to the expulsion region after it has traveled outwards over a length comparable to the distance between blocks at the micelle core surface $\xi \approx n_{PO}{}^{1/3} N^{-1/6}$. The residence time, T_R, of a copolymer in micelles roughly obeys the equation:

$$T_R \approx t_\xi \exp W \tag{5}$$

The pre-exponential factor t_ξ is the diffusion time for traveling over the distance ξ. The relevant friction in this motion is that of the collapsed hydrophobic block (the size of which is larger than ξ). Hence $t_\xi \approx n_{PO} N^{-1/3} \approx n_{PO}{}^{2/3}$ since N scales as n_{PO} for crew-cut micelles and as $n_{PO}{}^{4/5}$ for star-like micelles (see above). The rate constant for the copolymer exit writes:

$$k^- = 1/T_R \approx t_\xi^{-1} \exp(-W) \tag{6}$$

Triblock copolymers, as used in experiments, offer the exciting possibility for hydrophobic blocks to entangle upon mixing in the core. If entanglements occur during the residence time (evaluated without topological constraints) they should result in a marked reduction of k^-. Such a reduction seems not to be observed in the reported experiments. This may actually point towards poor mixing of the core blocks, a situation reminiscent of that of molten polymer rings, still a debated matter. In our case the "ring-like" structure is determined by the core/solvent interface where the junction points are confined. This encourages us to use the formula for effective diblock copolymers derived earlier. This expression has a few simple features supported by the data:

i) it is virtually independent of the polar block length;
ii) the activation energy W does not vary linearly with the hydrophobic block length, in marked contrast with conventional surfactants, and
iii) the final expulsion from the activated state is ruled by the local length scales, i.e., the globule radius R and ξ. As such the activation energy W depends on the quality of the solvent (i.e. the interaction energy between the solvent and the insoluble block) and hence on temperature. In a simplistic model both the polymer concentration in the globule and the surface tension γ depend on the reduced distance τ to the θ-temperature of the PO block ($\tau=(T-\theta)/\theta$; T=absolute temperature), which is the critical temperature for infinite chains: $\rho \approx \tau$ and $\gamma \approx \tau^2$ [37]. This should be questioned for water-soluble polymers but seems reasonable for moderate τ as in the present review. Regrouping the terms involving τ one obtains:

$$W = \exp \tau^{4/3} n_{\mathrm{PO}}^{2/3} \tag{7}$$

The values of τ have been calculated using for this purpose the estimated value $\theta=195$ K, obtained by extrapolating data from reported PPO/water phase diagrams [38,39]. Although the power of τ has only a moderate impact it significantly improves the quality of the fit of the data. Fig. 3 shows the variation of k^- with $\tau^{4/3} n_{\mathrm{PO}}^{2/3}$. The straight line going through the data points is the best fit of the data (quality of the fit characterized by the quantity $r^2=0.84$). The quality of the fit is much better than either that of k^- versus n_{PO} ($r^2=0.67$) or vs. $n_{\mathrm{PO}}^{2/3}$ ($r^2=0.69$), showing the importance and the necessity of the temperature correction.

4. Discussion and concluding remarks

The above discussion is restricted to the variation of the copolymer exit rate constant with the length of the hydrophobic block characterized by the degree of polymerization n_{PO}. However, the rate constant k^+ for the entry of a copolymer in micelles is expected to show a similar dependence because once a free copolymer collides with a micelle it can be considered as incorporated only after the hydrophobic globule uncoils and penetrates into the core. This unfolding and penetration will also involve the same energy W. This energy is responsible for the dependence of k^+ on n_{PO}.

The weak dependence of both k^+ and k^- on n_{EO} is not surprising as it is also observed with the nonionic conventional surfactants of the poly(ethylene oxide) monoalkyl ether type [3]. Here it reflects a weak dependency of the energy barrier against incorporation of the block copolymer into a micelle on the EO block.

Another point of interest concerns the value of the increment of free energy of transfer of a propylene oxide unit from micelle to water. This quantity cannot be obtained from the plot in Fig. 3. Indeed there is a prefactor in the exponential term and its value is not precisely known. There is also a prefactor before the exponential term, which depends only weakly on n_{EO}, as discussed above. The reported values of $\Delta G°_{\mathrm{tr}}$(PO) have been obtained from the slope of the plot of the lncmc of PEO–PPO–PEO copolymer at constant temperature against n_{PO}. The value reported by Wanka et al. [31] refers to 40 °C and involves data for copolymers with different n_{EO} values. Such a plot implies an unfolded conformation of the hydrophobic block, an assumption that is not supported by our results. We have plotted the cmc values of Wanka et al. against $n_{\mathrm{PO}}^{2/3}$ and obtained a linear fit of better quality than the original plot ($r^2=0.90$ vs. 0.87).

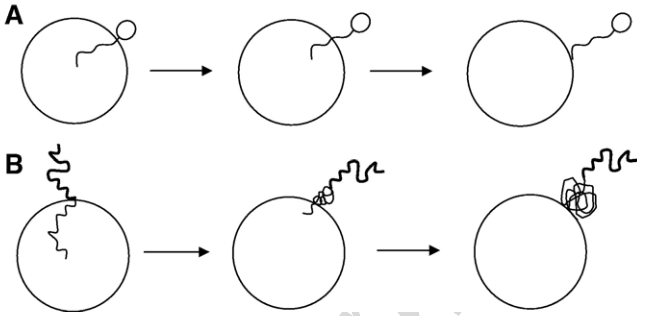

Fig. 4. Schematic representation of the entry/exit of (A) a surfactant and (B) a diblock copolymer into a micelle. A single surfactant/copolymer is represented for the sake of clarity. The part of the surfactant alkyl chain that is located out of the micelle is in full contact with water during the process, thus an interaction energy proportional to the number of carbon atoms in the alkyl chain. For the copolymer coiling into a globule occurs as it exits from the micelle. Contact between water and the hydrophobic repeat units occurs only at the surface of this globule, resulting in an interaction energy proportional to $n_{\mathrm{PO}}^{2/3}$.

Thermodynamic studies can be used to determine $\Delta G°_{\mathrm{tr}}$ (PO). This quantity can be obtained, for instance, from the variation of the partition coefficient of PPO oligomers between water and n-octanol, as a function of the degree of oligomerization. Oligomers must be used in order to avoid the coiling of the PO block in water.

One of the problems in the present work is that it concerned commercial PEO–PPO–PEO copolymers of unknown degree of purity. The authors hope that this work will stimulate other groups in preparing a series of purified amphiphilic copolymers, perhaps diblock PEO–PPO, all having the same EO block but PO blocks of increasing degree of polymerization and investigate the kinetics of copolymer exchange with the T-jump technique. No doubt that the results obtained in such a study would permit to reach more solid conclusions.

A last point that must be made before concluding is that the model of free copolymer supported by our results is that of a monomolecular micelle where the hydrophobic block is tightly coiled and contacts water only on its surface. In fact the PEO chain may fold over the PPO globule, resulting in a monomolecular micelle. Recall that such a model was postulated many years ago by Sadron [40]. Monomolecular micelle formation by block copolymers has been evidenced in many studies since that time.

To conclude, we summarize the similarities and differences between the kinetics of micelles of conventional surfactants and of amphiphilic block copolymers. Both micellar systems are characterized by similar relaxation behaviors with two relaxation processes assigned to the surfactant exchange and the micelle formation/breakdown. The characteristics of the copolymer exchange kinetics are, however, very different from those of the surfactant exchange kinetics. In particular, the entry rate constant of a surfactant is controlled by diffusion except for conventional surfactants with a very long alkyl chain and for gemini surfactants with an alkyl chain containing at least 12 carbon atoms. For copolymers the entry rate constant is slower to much slower than for a diffusion-controlled process and decreases very significantly as the length of the hydrophobic block is increased. While the residence time of a surfactant is an exponentially decreasing function of the number of carbon atoms in the surfactant alkyl chain, the residence time of a block copolymer is an exponentially decreasing function of the degree of polymerization, DP, of the hydrophobic block to the power 2/3. For conventional surfactants this dependence reflects a full contact between the free surfactant alkyl chain and water. For copolymers the $DP^{2/3}$ dependence comes from the coiling of the hydrophobic block in water that prevents to a large extent the contacts between hydrophobic units and water when the copolymer is not in the micelles. This is illustrated in the schemes in Fig. 4 that show the exit/entry process of a surfactant and a diblock copolymer into micelles.

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