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Water Self-Diffusion in Aqueous Block Copolymer Solutions

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ABSTRACT: The water self-diffusion in aqueous EO$_{99}$–PO$_{65}$–EO$_{99}$ (EO and PO being ethylene oxide and propylene oxide, respectively) solutions and gels has been studied with NMR. It was found that the water self-diffusion decreases monotonically with increasing polymer concentration, giving $D/D_0 \approx 0.5$ at 40 wt %. In the analysis of the data, using the cell diffusion model, it was found that the decrease in D/D_0 with increasing polymer concentration can be reproduced by taking into account both the obstruction due to excluded volume and the hydration of the polymer molecules. The analysis yields that somewhere between two and five water molecules per EO group are perturbed. On increasing the temperature, the water diffusion increases, following an Arrhenius-like equation, with E_A = 18.6 kJ/mol at 20 wt % and E_A = 17.8 kJ/mol at 8 wt %. Furthermore, the data are consistent with a gradual dehydration of the polymer molecules with increasing temperature. The dehydration, however, is uncorrelated with the occurrence of the gel region. We thus observe *no* anomalous dehydration of the polymer molecules on entering the gel region.

Introduction

In analogy with low molecular weight surfactants, many block copolymers form micelles in dilute solutions,[1,2] whereas at higher concentrations, liquid crystalline phases may occur.[3] This general behavior applies also to block copolymers of the EO$_a$–PO$_b$–EO$_c$ type (EO and PO being ethylene oxide and propylene oxide, respectively), which form micelles in dilute aqueous solutions, provided that the temperature is sufficiently high.[4–17] At higher polymer concentrations, and at intermediate temperatures, a "gel" region generally occurs.[16–23]

In a preceding paper, we have studied the temperature-dependent micellization of EO$_{99}$–PO$_{65}$–EO$_{99}$. In this experimental and theoretical study, it was found that the critical micellization concentration (cmc) decreases, and that the micellar size and aggregation number increase, all with increasing temperature.[24] Furthermore, the phase behavior of aqueous EO$_{99}$–PO$_{65}$–EO$_{99}$ solutions has been investigated.[16] It was found that a gel region appears at polymer concentrations above approximately 18 wt %, but only at intermediate temperatures (Figure 1). Thus, even a concentrated solution is relatively low-viscous at low and high temperatures. The upper temperature gel boundary was found to be significantly lower than the lower consolute temperature, the magnitude of the difference, however, depending on the polymer concentration. Moreover, the stability region of the gel is markedly affected by the presence of cosolutes, e.g., inorganic salts and hydrocarbons.[16]

From small-angle neutron scattering (SANS) experiments by Wanka et al.[17] and by Mortensen et al.,[20] it has been inferred that the gel consists of a close-packed (cubic) array of micelles. Furthermore, in one of their studies of EO$_{99}$–PO$_{65}$–EO$_{99}$, Rassing et al. found indications of temperature-dependent conformational changes, by using ^{13}C NMR[18], which was interpreted as a dehydration of the PPO core. A similar conclusion was drawn by Wanka et al., on the basis of DSC measurements.[17] Considering this, we were interested in investigating whether it was possible to observe this dehydration directly, by studying the water self-diffusion. In doing so, we use the FTPGSE-NMR technique,[25] which previously has been used for similar purposes.[25–27] In the interpretation of the diffusion data, we use the cell diffusion model, with which it is possible to take obstruction as well as "hydration" effects into account,[28] and which has previously been used for studying the hydration of nonionic surfactants.[39]

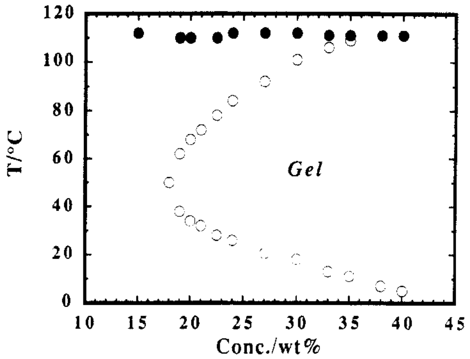

Figure 1. Phase behavior of the EO$_{99}$–PO$_{65}$–EO$_{99}$/water system. The solid circles refer to the lower consolute curve.

Experimental Section

Self-Diffusion. The ^{1}H FTPGSE technique was used to obtain the self-diffusion coefficients.[25] In this technique, one uses a 90°–τ–180°–τ–echo pulse sequence, with two additional rectangular magnetic field gradient pulses of magnitude G, separation Δ, and duration δ. One can show that the echo amplitude (A) at $t = 2\tau$ is given by[29]

$$A(2\tau) = A(0) \exp[-2\tau/T_2 - \gamma^2 G^2 D \delta^2 (\Delta - \delta/3)] \qquad (1)$$

where T_2 is the transvere relaxation time and γ is the magnetogyric ratio. In this work the diffusion coefficients D were obtained by measuring the echo amplitude as a function of δ, keeping the other parameters fixed. The NMR spectrometer used was a JEOL FX-60, operating at 60 MHz.

Material. In the experiments, we used a specially purified sample of Pluronic F127, which was kindly supplied by BASF Wyandotte, USA. This polymer has a total molecular weight of 12 500, and consists of approximately 70% PEO; i.e. its formula is EO$_{99}$–PO$_{65}$–EO$_{99}$. NMR spectra confirm that the ratio PEO/PPO is approximately 70/30. No impurities were observed in these spectra.

Results

In Figure 2, the self-diffusion coefficient (D) of water (relative to the self-diffusion coefficient of neat water, D_0) is shown as a function of the polymer concentration. We observe that D/D_0 decreases monotonically with increasing polymer concentration. At 40 wt %, $D/D_0 \approx 0.5$. In

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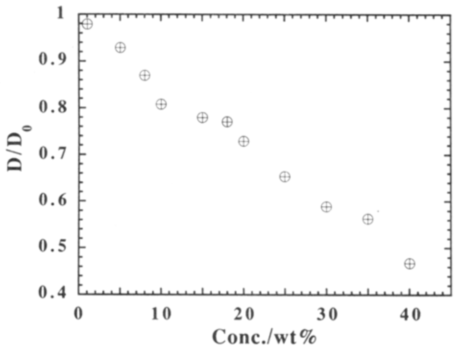

Figure 2. Concentration dependence of the self-diffusion coefficient of water in the aqueous polymer solution (D), relative to the diffusion coefficient in neat water (D_0) at 27 °C. The gel boundary at this temperature is 22 wt %.

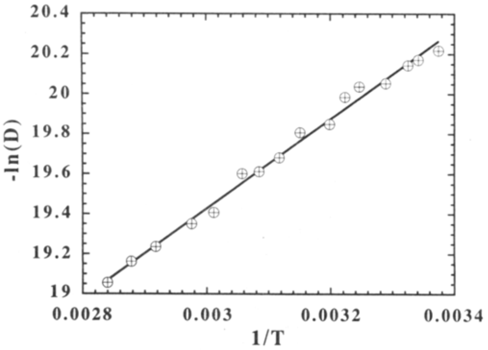

Figure 3. Temperature dependence of the water self-diffusion in a 20 wt % polymer solution. The gel boundaries at this polymer concentration are 34 and 68 °C (0.00326 and 0.00293 K^{-1}).

particular, we observe no abrupt changes in D/D_0 as we enter the gel region (cf. Figures 1 and 2).

In Figure 3, the temperature dependence of the water self-diffusion in a 20 wt % polymer solution is shown. As can be seen in this figure, the water diffusion increases with increasing temperature. More specifically, the temperature dependence of the water diffusion follows an Arrhenius-like equation with an activation energy for diffusion of approximately 18.6 kJ mol^{-1}, which is about the same as in an 8 wt % solution (17.8 kJ mol^{-1}, results not shown) and in pure water (17.6 kJ mol^{-1}).[30]

Discussion

General Remarks. In studies of the diffusion of small molecules in polymeric systems, it is generally found that the diffusion of these substances is remarkably little affected by the presence of the polymers, even at quite high polymer concentrations.[31] As can be seen in Figure 2, this is the case in the present system as well. Thus, D/D_0 decreases monotonically with increasing polymer concentration, but remains quite high, even at high polymer concentrations ($D/D_0 \approx 0.5$ at 40 wt %).

The reason for the decrease in D/D_0 with the polymer concentration is 2-fold. Firstly, the presence of impermeable polymeric obstacles in the solution increases the average pathway for a diffusing water molecule, which is equivalent to a decrease in the self-diffusion coefficient. Secondly, the diffusion of the water molecules is reduced through the hydration of the polymer molecules.

Model. In order to consider both effects of specific solute–solvent interactions and effects due to the excluded volume on the solvent diffusion in colloidal solutions, Jönsson et al. developed the cell diffusion model.[28] In this model, the macroscopic system is divided into a number of cells, which, in turn, can be further subdivided.

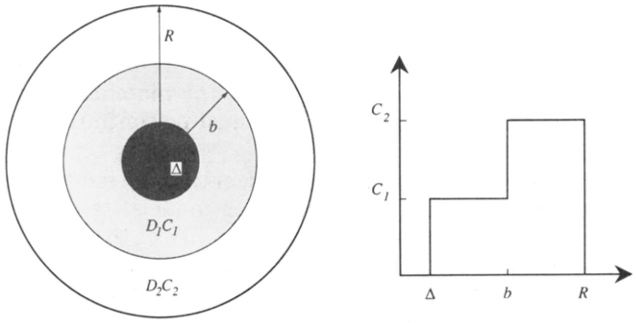

Figure 4. A two-dimensional cut through the cell described in the text. The central region represents the micellar core, which is assumed to be unsolvated. The shadowed area represents the micellar palisade, with the mean concentration and diffusion properties C_1 and D_1 (D^{w}_{palisade}), while the white area denotes the bulk solution, with the concentration C_2 and the diffusion D_2. Shown also is the assumed concentration profile for the solvent.

However, contrary to many other applications of the cell model, the cell diffusion model considers the flow of molecules within the system, which makes the boundary conditions more difficult to find. However, these were found from considerations of irreversible thermodynamics.

The effective diffusion coefficient D_i^{eff} for species i diffusing in a system of spherical cells is given by

$$D_i^{\text{eff}} = \frac{D_i(R)\,C_i(R)\,U_i(R)}{\langle C_i \rangle} \tag{2}$$

where R represents the cell radius, $D_i(R)$ and $C_i(R)$ represent the diffusion coefficient and the concentration of i at the wall boundary, respectively, and $\langle C_i \rangle$ represents the average cell concentration. $U_i(R)$ is a function introduced to obtain a simple formalism, and is obtained from

$$r\frac{dU_i}{dr} = (1 - U_i)(2 + U_i) - rU_i\frac{d}{dr}\{\ln\,[D_i(r)\,C_i(r)]\} \tag{3}$$

It can be shown that $U_i(r)\,D_i(r)\,C_i(r)$ is a continuous function for all r and that $U_i(0) = 1$. In principle, eq 2 may be solved for any C_iD_i profile to obtain an effective self-diffusion coefficient for i. However, for simplicity, we will only consider the special case, where C_iD_i is constant, although with different values in different regions of the cells. For a two-region cell (b being the radius of the inner region of the cell); i.e.

$$D_i(r)\,C_i(r) = D_1C_1 \qquad r < b \tag{4}$$

$$D_i(r)\,C_i(r) = D_2C_2 \qquad r > b$$

$U(R)$ is given by

$$U(R) = \frac{1 - \beta\phi}{1 + \beta\phi/2} \tag{5}$$

where

$$\phi = b^3/R^3 \tag{6}$$

and

$$\beta = \frac{D_2C_2 - D_1C_1}{D_2C_2 + D_1C_1/2} \tag{7}$$

The two-region model, however, oversimplifies a real micellar system, since part of the solvent molecules interact with the headgroup shell and thus do not behave as in the bulk solution. In this case, a third region, representing the headgroup shell, must be introduced (Figure 4).

However, this offers no problems in the evaluation of the effective diffusion coefficient. In fact, any number of shells may be accounted for by a successive use of eq 5, since the solutions from different regions may be matched using the restriction that $U(r)\,D(r)\,C(r)$ must be continuous at all points in the cell.

From the discussion above, it is clear that the model has the advantage, compared to earlier models, that it is possible to take into account the mobility of the solvent molecules within the solvated headgroups of the aggregates. Moreover, it is possible to take the finite diffusion of the aggregates (cells) into account.[28]

In order to calculate the water self-diffusion in this particular system, we subdivide each cell into three different regions according to Figure 4. As can be seen in this figure, we assume a spherical symmetry of the aggregates. This is probably correct at low polymer concentrations, as indicated by the small hydrodynamic radius,[6,16,17] as well as the symmetric scattering,[6,17,20] obtained for this system. In concentrated systems, this assumption is more uncertain, although Wanka et al.[17] found that the polymer micelles remain small even in the gel region. Furthermore, due to the similarity in the solvent obstruction for spheres and even quite large prolate-shaped aggregates,[28] this assumption can be made without introducing any serious errors.

As can be seen in Figure 4, the aggregates are assumed to consist of a PPO core, surrounded by a PEO palisade. Furthermore, we assume the PPO core to be completely expelled from water, i.e., completely unsolvated. The palisade layer, on the other hand, is characterized by an average water concentration (C_1), and an average diffusion coefficient (D_1 or $D^{w}_{palisade}$). The remaining volume of the cell consists of bulk water of concentration C_2, diffusing with diffusion coefficient D_2.

In the calculations, D_2 is set as a constant, equal to the water self-diffusion at the cmc, which for this particular system is taken to be 1 wt %.[24] Since it is generally found that cmc decreases with increasing temperature in aqueous solutions of both low molecular weight nonionic surfactants and PEO–PPO–PEO block copolymers, this value constitutes an *upper* limit.[24,32,33] Furthermore, since the polymer concentration in our system is high, the actual value of the cmc is of minor importance. This was further confirmed in control calculations at various values of the cmc (results not shown).

Moreover, we have assumed the cells to be immobile. This is a reasonable assumption, since the polymer diffusion ($\sim 10^{-11}$–10^{-12} m^2/s) is much slower than the water diffusion ($\sim 10^{-9}$ m^2/s)[16]. As has been shown previously,[28,39] the total effective diffusion coefficient D_i of compound i in a micellar system may be written as

$$D_i = D_i^{\mathrm{eff}}[1 - D_{\mathrm{micelle}}/D_i^{\circ}] + D_{\mathrm{micelle}} \qquad (8)$$

where D_i^{eff} is the effective self-diffusion coefficient in a cell centered around the micelle, D_i° the self-diffusion coefficient of the neat solvent, and D_{micelle} the self-diffusion coefficient of the micelle. Control calculations, based on eq 8, show that this assumption gives an error of only 1–2%. No assumptions are made concerning the aggregation number of the micelles. Instead, the calculations are based solely on volume fractions. For this purpose, we need to know the volume of the water molecules (taken to be 30 Å^3), and of the EO and PO groups (taken to be 65 and 96 Å^3, respectively, as obtained from the densities of the PEO and PPO in their amorphous states).[34,35]

Effects of Polymer Concentration. We are now in the position of analyzing our self-diffusion data. In Figure 5, we show D/D_0 as a function of the polymer concentration. In the same figure, we show the calculated values of D/D_0 at different values of C_1, assuming that $D_1 = 0$. As we can see, the pure obstruction effects ($C_1 = 0$) are far from able to account for the observed decrease in D/D_0 with increasing polymer concentration. Instead, it is clear that there are somewhere between 1.75 and 2.75 water molecules bound ($D_1 = 0$) to every EO group, which is in good agreement with what has previously been found for PEO, as well as for nonionic surfactants of the type C_mE_n.[27,36]

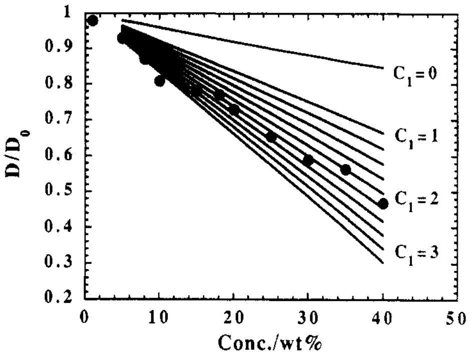

Figure 5. Comparison between experimental values of D/D_0 at different polymer concentrations and theoretical predictions for different values of the number of water molecules completely immobilized in the palisade layer. The gel boundary is 22 wt %.

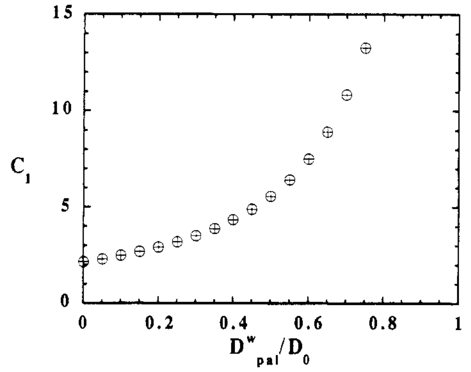

Figure 6. Connected values of C_1 and $D^{w}_{palisade}/D_0$ for a 40 wt % solution at 27 °C.

It is interesting to note that there is *no* dehydration on entering the gel region by increasing the polymer concentration. Instead, the entire decrease in D/D_0 with increasing polymer concentration can be reconstructed with a constant number of water molecules bound per EO group. This result seems to be in contrast to the findings of both Rassing et al.[18] and Wanka et al.,[17] who inferred that the main driving force for the gelation is a temperature-dependent dehydration of the PPO cores.

Naturally, the notion of the water molecules being either bound or free is very crude. Instead, we would expect the water molecules to be retarded by the EO groups, but not completely bound to them. This is further supported by NMR relaxation studies of water in micellar solutions of nonionic surfactants of the type C_mE_n.[36] Making the full calculation of connected values of C_1 and the diffusion of water in the palisade layer ($D^{w}_{palisade}/D_0$) results in Figure 6. We see that the case of $D^{w}_{palisade} = 0$ constitutes the lower limit of C_1. Allowing a more unretarded diffusion of the water molecules in the palisade layer results in an increase in the number of obstructed water molecules needed to accomplish the observed value of D/D_0, or conversely, if more water is present in the palisade layer, they necessarily become less perturbed.

It is difficult to know exactly which of the connected values of C_1 and $D^{w}_{palisade}/D_0$ describe the system most

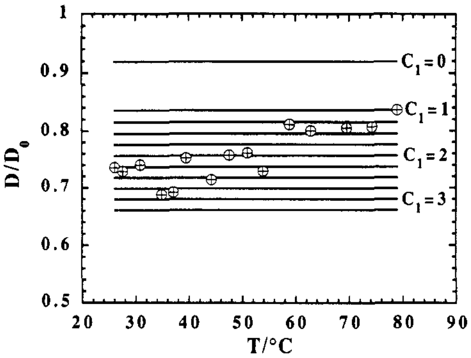

Figure 7. Comparison between experimental values of D/D_0 at different temperatures and theoretical predictions for different values of the number of water molecules completely immobilized in the PEO palisade layer. The polymer concentration was 20 wt %. The gel boundaries at this polymer concentration are 34 and 68 °C.

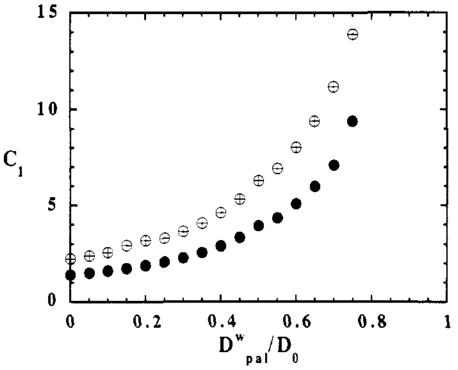

Figure 8. Connected values of C_1 and $D^{w}_{\mathrm{palisade}}/D_0$ for a 20 wt % solution at 28 (crossed circles) and 63 °C (filled circles). The gel boundaries at this polymer concentration are 34 and 68 °C.

correctly, especially since both C_1 and $D^{w}_{\mathrm{palisade}}/D_0$ must be considered as averages of the corresponding radial distributions. However, taking $D^{w}_{\mathrm{palisade}}/D_0$ to be 0.5 as a reasonable upper limit of the water diffusion in the palisade layer,[36] we conclude that somewhere between two and five water molecules per EO group are perturbed by hydration at this temperature (27 °C).

Effects of Temperature. Following the discussion above, we wanted to evaluate, from our data of the temperature dependence of the water diffusion of a concentrated sample (20 wt %), how C_1 changes with temperature, and, especially, how this correlates with the phase behavior. The results of these calculations are shown in Figure 7. As is clearly shown in this figure, there is indeed a dehydration of the palisade on increasing the temperature. The decrease, however, is gradual and moderate, with no abrupt changes at the onset of gelation. Instead, the dehydration that does occur at higher temperature more resembles the gradual dehydration that has been observed previously for PEO and for nonionic surfactants of the type C_mE_n.[27]

In the calculations of the dependence of C_1 on temperature, we have assumed that $D^{w}_{\mathrm{palisade}} = 0$, again rendering the obtained values of C_1 lower limits of the number of water molecules in the palisade layer. Making the full calculations, i.e., plotting connected values of C_1 and $D^{w}_{\mathrm{palisade}}/D_0$ for a 20 wt % solution at a few different temperatures, results in Figure 8. We see that, whatever the state of hydration, the EO groups are indeed slightly dehydrated at a higher temperature. Depending on the degree of binding, however, different values of the change in C_1 are obtained.

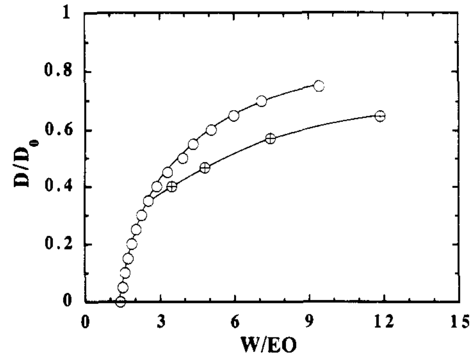

Figure 9. Comparison between the water self-diffusion in solutions of PEO and of the block copolymer. D^{w}_{PEO}/D_0 is plotted vs the number of water molecules per EO group (as given by the composition, crossed circles)[37] while $D^{w}_{\mathrm{palisade}}/D_0$ is plotted vs C_1 (open circles). The temperature was 66 °C.

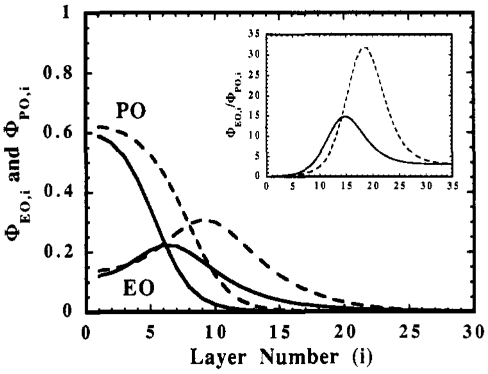

Figure 10. Calculated segment volume fraction ($\Phi_{\mathrm{EO},i}$ and $\Phi_{\mathrm{PO},i}$) versus layer number (i) at a polymer volume fraction of 0.050 at T = 304.9 K (at the cmc, solid lines) and at T = 324 K (above the cmc, dashed lines). The inset shows the volume fraction ratio ($\Phi_{\mathrm{EO},i}/\Phi_{\mathrm{PO},i}$) at 304.9 (solid line) and 324 K (dashed line).[24]

If we assume that the palisade behaves as a homogeneous PEO solution with respect to water diffusion, we may get some further information on the state of hydration. If the assumptions above are reasonable, it should be possible to compare the $D^{w}_{\mathrm{palisade}}/D_0$ vs C_1 curve with experimental values of D^{w}_{PEO}/D_0 vs $C_{1,\mathrm{PEO}}$, i.e., the water self-diffusion coefficient in the PEO solution and the number of water molecules per EO group as given by the global composition, respectively. It follows that the values of $D^{w}_{\mathrm{palisade}}/D_0$ and C_1 that most correctly describe the situation in the block copolymer solution should coincide at some point with the D^{w}_{PEO}/D_0 vs $C_{1,\mathrm{PEO}}$ line. Thus, the intersection point between the two curves represents the best values of $D^{w}_{\mathrm{palisade}}/D_0$ and C_1, under the conditions imposed.

In Figure 9, we show the result of such a comparison at 66 °C. The polymer concentration used was 20 wt %, but the results obtained should equally well describe the situation at other polymer concentrations (cf. the concentration-independent hydration numbers obtained in Figure 5). We see that only at low values of C_1 ($C_{1,\mathrm{PEO}}$) do the two curves coincide, which shows that, at this temperature, approximately 2–3 water molecules per EO group are perturbed by hydration, and that these water molecules are rather mobile ($D^{w}_{\mathrm{palisade}}/D_0 \approx 0.2$–$0.3$).

As discussed above, the Pluronic micelles are approximated by a core–palisade model, where the core is assumed to consist of (unhydrated) PPO only, whereas the palisade is thought to consist of hydrated PEO. Obviously, this model is a very crude one. Using a more refined model (cf. ref 24), we obtain segment density distributions of EO and PO groups, as illustrated in Figure 10. In short, the calculations were performed using a spherical lattice. A single micelle might be formed in the center of the lattice at a specified bulk polymer concentration (chemical potential). The calculations involve a self-consistent determination of the volume fractions of all species in each layer of the heterogeneous system. Given the distributions of volume fractions and internal states (cf. ref 24), the free energy of forming a micelle at a fixed position may be calculated. At equilibrium, this free energy is balanced by the favorable translational entropy. This requirement makes it possible to evaluate the micellar concentration and the micellar aggregation number. A description of the equations relevant for the calculations is given in ref 40.

From Figure 10, we see that the PO groups are indeed primarily located in the inner part of the micelles, whereas the EO groups are primarily located in the outer regions of the micelles, in agreement with our assumptions. However, the segment density distributions of both EO and PO vary quite smoothly with the radius, in contrast to the assumptions. Furthermore, the segregation between EO and PO groups is far from complete, and the core of the micelles contains 15% EO. Moreover, the model calculations predict that even the center of the micelles contains 25% water. This, however, should not be taken as an indication of the core of the Pluronic micelles being hydrated. Instead, it has been demonstrated previously that this type of mean-field lattice theory exaggerates the water content in hydrophobic regions, e.g., in lecithin bilayers, which from experiments are known to be essentially void of water.[38] At higher temperatures, there is a growth of the micelles, resulting in the segment density distributions of both EO and PO being displaced to larger radii. Furthermore, with increasing temperature, the tendency for segregation increases, as illustrated in the inset of Figure 10. Moreover, there is no major dehydration of the micelles at higher temperatures, which is in line with our experimental findings, but at variance with the results of Wanka et al.[17] and Rassing et al.[18]

From the discussion above, it is clear that the core–palisade model is a very crude one. However, although a more sophisticated model provides a more detailed and realistic picture of the structure of the micelles, it is not likely to provide much additional information on the state of hydration in these systems. The reason for this is that the water self-diffusion is likely to depend only weakly on the detailed shape of the segment density profile of the micelles.

Conclusions

The water self-diffusion in aqueous EO_{99}–PO_{65}–EO_{99} solutions and gels has been studied by NMR and analyzed by means of the cell diffusion model. It was found that the diffusion data can be accounted for by assuming that somewhere between one and five water molecules per EO group are perturbed, depending on the temperature. This is in good agreement with previous findings on PEO, as well as nonionic surfactants of the type C_mE_n. There are no indications of dehydration on entering the gel region by increasing the polymer concentration at a fixed temperature. On increasing the temperature, there is a decrease in the number of water molecules perturbed by the polymer. However, the decrease is small and gradual, and *uncorrelated* to the occurrence of the gel region.

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