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Small-Angle Neutron Scattering Characterization of Micelles Formed by Poly(dimethylsiloxane)-graft-polyether Copolymers in Mixed Polar Solvents

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The self-assembled structure of an amphiphilic poly(dimethylsiloxane)-graft-polyether copolymer has been investigated in binary solvents consisting of water and one of the following polar organic solvents: 2-propanol, ethanol, formamide, or glycerol. Micelle structural parameters were obtained by fitting the core−corona form factor and hard-sphere interaction structure factor to small-angle neutron scattering (SANS) data obtained at contrast conditions where the solvents were fully deuterated and the copolymer was not. The siloxane copolymer forms in water at 20 °C micelles that consist of a “dry” core with a radius of about 6 nm and a solvated (about 40% polymer) corona with a thickness of 2 nm; the relatively thin corona may be due to the comb-type architecture of the siloxane copolymer. The micelle radii, micelle core radii, micelle association numbers, and polymer volume fractions in the micelle core and corona decreased with increasing cosolvent/water ratio in the mixed solvents containing 2-propanol, ethanol, or formamide. On the contrary, the addition of glycerol led to an increase of the micelle association number. The above findings are discussed in terms of the relative location of the polar organic solvents in the interior or exterior of the siloxane copolymer micelles. In particular, the micelle association numbers observed for different water−cosolvent mixtures can be correlated to the octanol−water partition coefficients of the respective cosolvents. A transition from spherical to ellipsoid micelles was observed upon an increase in the temperature: this is attributed to the desolvation of the polyether chains. This structural transition correlates with the solvent quality in the mixed solvents: ethanol and 2-propanol, which solvate the interior of the micelles, tending to keep the micelles spherical, while increased glycerol content in the mixed solvent leads to the formation of ellipsoids at a fixed temperature.

Introduction

Amphiphilic molecules containing poly(dimethylsiloxane) (silicone) are used as wetting and foaming/defoaming agents in numerous applications ranging from the production of polyurethane foam to that of cosmetics, agricultural adjuvants, textiles, and coatings.[1−6] Recently, the self-assembly behavior in water of a number of low molecular weight trisiloxane−ethoxylate surfactants and higher molecular weight block and graft poly(dimethylsiloxane)-containing copolymers has been reported.[7−12] Rake-type siloxane surfactants, such as $MD_{22}D'_2M$ (where, $M = Me_3SiO_{1/2}-$, $D = -Me_2SiO-$, $D' = Me(R)SiO-$, $R = -(CH_2)_3-O-(EO)_{12}-H$, and EO = ethylene oxide), can form at low concentrations (e.g., 5%) in water an unusual diversity of spheroidal and elongated micelles, as well as tubelike, unilamellar and mutilamellar vesicles.[13] At high concentrations (e.g., >50%) in water, silicone-containing surfactants[9,10] and block copolymers[11] can form various ordered lyotropic liquid crystalline structures.

An important factor controlling the structure of micelles and ordered structures formed by amphiphilic block or graft copolymer is the solvent quality.[14] This has been exemplified by work carried out recently in our group on poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) block copolymers (commercially known as Poloxamers or Pluronics) where water is typically used as a solvent (being selective for PEO). In such systems, the addition to water of common salts[15] or polar organic solvents,[16−19] such as glycerol, ethanol, and formamide, provides extra degrees of freedom in tailoring the solution properties for specific applications. The addition of polar organic solvents also causes pronounced effects on the concentration range of stability of the various lyotropic liquid crystals formed by PEO−PPO−PEO block copolymers in water and on the characteristic length scales of the ordered structures.[20−22] It is notable that the same trends that are observed in the PEO−PPO−PEO block copolymer micelle structural parameters (obtained by fitting a model for the micelle structure to small angle neutron scattering data) upon the replacement of part of the water by a certain polar organic solvent[19] are also observed in the variation of the spacing in lyotropic liquid crystalline structures (obtained directly from small-angle X-ray scattering).[20] Another case-study of morphological control of block copolymer self-assembly by means of mixed solvents has been presented by Eisenberg and coworkers.[23,24] They found that an increase of the water content in mixtures with *N*,*N*-dimethylformamide transforms the enthalpy-driven (typical of block copolymers in apolar organic solvents) micellization of polystyrene-poly(acrylic acid) diblock copolymers to an entropy-driven process (typical of amphiphiles in water).[23] With increasing water content in a water-dioxane mixture, a sequence of structures formed by polystyrene−poly(acrylic acid) was observed, that followed the order of single chains, spheres, sphere and rod mixtures, rods, rod and vesicle mixtures, and finally pure vesicles.[24]

Despite the progress outlined above, the published information on the effects of polar organic solvents on the solution behavior

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of water-soluble amphiphilic copolymers, such as the subject of this study, is still limited. Such lack of fundamental knowledge is in contrast with the current trend of increased use of functional polymers as pharmaceutical excipients, in personal care products, detergents, and foods. Another emerging application where such knowledge is useful is the synthesis of nanostructured materials templated by amphiphiles. For example, the type and amount of alkanol added have been shown to affect both the pore diameter and the pore wall thickness in mesoporous silica templated by PEO−PPO−PEO block copolymer lyotropic liquid crystals.[25] Further study is required in order to obtain detailed information on the solvent partitioning in the self-assembled structure and on the solvation of the hydrophobic and hydrophilic segments when polar organic solvents are present in aqueous solutions. To this end, we have initiated an investigation of the self-assembly of an amphiphilic poly(dimethylsiloxane)-graft-polyether copolymer in mixed solvents consisting of water and water-miscible polar organic solvents[26] (selected on the basis of fundamental considerations and/or in terms of their usage in pharmaceutics, inks, or coatings). The type of organic solvent present in the mixed solvent affected greatly the siloxane copolymer concentration where micelles start forming (CMC), thus providing indirect evidence on the solvent effects.[26]

To obtain direct information on the solvent effects on the micelle structure, we carried out small-angle neutron scattering (SANS) experiments on this poly(dimethylsiloxane)-graft-polyether copolymer in binary solvents consisting of water and one of the following: ethanol, 2-propanol, formamide, or glycerol. SANS has been shown very useful in probing solvent effects on the structure of micelles formed by PEO−PPO−PEO block copolymers[18,19] and by nonionic ethoxylated surfactants.[27,28] The variables that we examined include the content of the polar organic solvent in the mixed solvent and the temperature; the siloxane copolymer concentration was kept constant at a value well above the concentration where micelle start forming. By fitting appropriate form and structure factors to the scattering data, micelle structural parameters, such as core radii, micelle radii, micelle association number, and polymer volume fraction in the core and corona are obtained. From these, the role of the polar organic solvent on the siloxane copolymer self-assembly is deduced. A sphere-to-ellipsoid shape evolution of micelles observed at elevated temperatures and/or under certain solvent conditions is also connected to the solvent effects. The study reported here adds to the very small number of studies that have employed SANS to study the self-assembly of siloxane surfactants or copolymers,[7,12] or have addressed the structure of micelles in mixed solvents.[18,19,27,28]

Materials and Methods

Materials. The poly(dimethylsiloxane)-graft-polyether copolymer examined here was provided by Goldschmidt AG, Essen, Germany, and has the nominal chemical formula $MD_{70}D'_5M$ (where $M = Me_3SiO_{1/2}-$, $D = -Me_2SiO-$, $D' = Me(R)SiO-$, and $R =$ PPO−PEO polyether) with MW = 11500. The molecular weight per polyether side chain is 1200 and its composition is 75% PEO and 25% PPO. The polyether side chains are distributed randomly along the poly(dimethylsiloxane) backbone. In this siloxane copolymer 11% free polyether was present due to an excess polyether used in the synthesis; this is common for such siloxane-polyether copolymers.[13] The presence of the free polyether in solution is not expected to affect the siloxane copolymer micelle structure since the polyether has sufficiently low molecular weight and sufficiently high PEO content to be completely water-soluble;[29] however, the free polyether is expected to contribute to the background scattering. For the neutron scattering experiments we used deuterated water (D_2O), deuterated 2-propanol ($CD_3CDODCD_3$), deuterated ethanol (CD_3CD_2OD), deuterated formamide ($DCOND_2$), and deuterated glycerol ($CD_2ODCDODCD_2OD$) purchased from Cambridge Isotope Laboratories Inc. (Andover, MA). Care was taken to avoid exposure of the organic solvents to atmospheric humidity prior to their addition to water. The solvents were mixed on a volume basis while the siloxane copolymer was added on a weight basis.

Small-Angle Neutron Scattering Experiments. SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research, beam guide NG3.[30] The neutron wavelength used was $\lambda = 0.6$ nm. The sample to detector distance used was 260.0 and 1300.0 cm. The resolution ($\Delta q/q$) was about 0.15. The angular distribution of the scattered neutrons was recorded in a two-dimensional detector; the radial average was subsequently obtained and used for data analysis. Siloxane copolymer solutions (5 wt %) were used to investigate the micelle structure. The compositions of the D-solvent−D_2O mixed solvents examined here were 0, 20, 40, and 60 vol % formamide; 0, 10, and 20 vol % ethanol, 2-propanol, or glycerol. The samples were placed in 1 mm path length stoppered "banjo" quartz cells and scattering data were recorded at temperatures ranging from 20 to 60 °C. Adequate time was allotted for thermal and kinetic equilibration. Scattering intensities from the siloxane copolymer solution were corrected for detector background, empty cell scattering, and sample transmission. The resulting corrected intensities were normalized to absolute cross section units.[30] This way we can obtain intensities on an absolute scale.

SANS Data Analysis: Micelle Structure. The absolute SANS intensity can be expressed as a product of the form factor$P(q)$ and the structure factor $S(q)$:

$$I(q) = NP(q)S(q) \tag{1}$$

where N is the number density of the scattering particles: in our case, micelles. The form factor $P(q)$ accounts for the intramicelle structure. Several models have been proposed for the form factor of block copolymer micelles; the ones relevant to this study are summarized here. Note that the references cited below are representative of work performed on PEO−PPO−PEO block copolymer micelles in aqueous solution, and they do not constitute a complete list. The simplest form factor that describes a micelle with a well-defined core devoid of (deuterated) solvent is that of a hard sphere.[31,32] However, most block copolymer micelles are recognized as having a core−corona structure. A way to account for this is to have a form factor consisting of a spherical core and a corona layer of a given thickness, with the polymer/solvent content across the corona thickness to be constant (but adjustable); in this model there is a step change in the solvent concentration at the core−corona and at the corona-solution interfaces.[33,34] A variation of this theme is a form factor that considers a hard sphere to describe the micelle core and Gaussian chains to describe the micelle corona.[35] A recent improvement is the so-called cap-gown form factor where the micelle core is again a hard sphere but the corona consists of a Gaussian distribution of polymer segments with no abrupt boundary between the micelle core and the solvent.[36] Perhaps the best approach would be to use no model for the micelle structure at all, but to extract the scattering density correlation function using the generalized indirect Fourier transformation (GIFT) method developed by Glatter.[37]

However, the GIFT method is computationally involved compared to form factors for which analytical expressions are available. Note that when the GIFT method was applied to PEO−PPO−PEO block copolymer micelles, the results were indicative of spherical micelles, relatively monodisperse in size.[37]

In this work we use the core−corona form factor model to describe the structure of the micelles formed by the poly(dimethylsiloxane)-graft-polyether copolymer in mixed solvents.[33,34] Our selection is based on the premise that, for a relatively unknown system, such as the one we consider here, one is on solid ground when using a well-tested form factor that is expressed by explicit analytical equations and that captures the salient features (i.e., core−corona structure) of the micelle structure. In recent work, we have found the core−corona form factor very useful for describing mixed solvent effects on the micelle structure of PEO−PPO−PEO block copolymers;[18,19] the core−corona form factor has also been used to fit data from ethoxylated surfactant micelles in mixed solvents.[27,28] In particular, the core−corona form factor is based on the contrast (i) between the polymer-rich micelle core and the micelle corona of intermediate polymer concentration and (ii) between the micelle corona and the solvent-rich surroundings, thus allowing for different solvent contents in the micelle core and corona:

$$P(q) = \{(4\pi R_{\mathrm{core}}{}^3/3)(\rho_{\mathrm{core}} - \rho_{\mathrm{corona}})[3J_1(qR_{\mathrm{core}})/(qR_{\mathrm{core}})] + (4\pi R_{\mathrm{micelle}}{}^3/3)(\rho_{\mathrm{corona}} - \rho_{\mathrm{solvent}})[3J_1(qR_{\mathrm{micelle}})/(qR_{\mathrm{micelle}})]\} \quad (2)$$

Here R_{core} and R_{micelle} are the radii of the micelle core and whole micelle, respectively; ρ_{core}, ρ_{corona}, and ρ_{solvent} are the scattering length densities (SLD) of the core, corona, and solvent (assuming a homogeneous solvent distribution in each of the domains); $J_1(y)$ is the first-order spherical Bessel function. In fitting the core−corona model to the scattering data, we view the micelles as consisting of a core composed of siloxane and PPO segments (with little or no solvent present) and a relatively solvated corona where the PEO segments reside. The SLD of the core, ρ_{core}, and that of the corona, ρ_{corona}, are then a function of the average (over the core radius and over the corona thickness) volume fraction of siloxane and PPO segments in the core (α_{core}) and of the average volume fraction of PEO in the corona, respectively:

$$\rho_{\mathrm{core}} = \alpha_{\mathrm{core}}\rho_{\mathrm{hydrophobic}} + (1 - \alpha_{\mathrm{core}})\rho_{\mathrm{solvent}}$$
$$\rho_{\mathrm{corona}} = \alpha_{\mathrm{corona}}\rho_{\mathrm{PEO}} + (1 - \alpha_{\mathrm{corona}})\rho_{\mathrm{solvent}} \quad (3)$$

where $\rho_{\mathrm{hydrophobic}}$ ($=0.1 \times 10^{10}$ cm^{-2}) is the SLD of siloxane plus PPO (where $\rho_{\mathrm{siloxane}}=0.0658 \times 10^{10}$ cm^{-2} and $\rho_{\mathrm{PPO}} = 0.325 \times 10^{10}$ cm^{-2}), ρ_{PEO} ($=0.547 \times 10^{10}$ cm^{-2}) is the SLD of PEO, and ρ_{solvent} is the SLD of the water−polar organic solvent mixture ($\rho_{\mathrm{D2O}} = 6.33 \times 10^{10}$ cm^{-2}, $\rho_{\mathrm{D-2-propanol}} = 6.22 \times 10^{10}$ cm^{-2}, $\rho_{\mathrm{Dethanol}} = 5.95 \times 10^{10}$ cm^{-2}, $\rho_{\mathrm{Dformamide}} = 6.34 \times 10^{10}$ cm^{-2}, and $\rho_{\mathrm{Dglycerol}} = 7.48 \times 10^{10}$ cm^{-2}).[30] Our use of the siloxane and PPO SLDs to determine the SLD of the micelle core and of the PEO SLD to determine the SLD of the micelle corona does not preclude the presence of small amounts of PEO in the core and/or of small amount of siloxane and PPO in the corona region; this is because the SLDs of the hydrogenated polymer species (siloxane, PPO, and PEO) are very different than those of the deuterated solvents. Also, our use of the initial (fixed) water−polar organic solvent composition in determining the SLD of the solvent in the micelle core, micelle corona, and micelle-free solvent regions, does not preclude different ratios of cosolvent/water to exist in each of the three regions (again, because the SLD values of the deuterated solvents are similar to each other relative to the SLD of the polymer); in fact, we have reasons to believe that for some cosolvents there is partitioning of the cosolvent inside the micelle.[19]

The volume fraction of polymer in the core (α_{core}) and the volume fraction of polymer in the corona (α_{corona}) can be expressed in terms of the core and micelle radii (R_{core} and R_{micelle}) and the micelle association number, N_{assoc}, i.e., the number of copolymer molecules which (on the average) participate in one micelle.[19] R_{core}, R_{micelle}, and N_{assoc} are the parameters used to fit the core−corona form factor for the SANS data. The R_{core}, R_{micelle}, N_{assoc}, α_{core}, and α_{corona} parameters extracted from the model fits to our data, while accurate for the model used here (a variation of more than ±1 in the values of R_{core}, R_{micelle}, and N_{assoc} would result in a discernible worsening of the model fit to the experimental data), are dependent on the choice of model used to fit the data, as different models use different physical descriptions for the fitting parameters. However, the physical picture that emerges for the micelle (when one considers the parameters obtained from fitting in the context of the specific model) ought to be independent of the model used. This has been indeed the case for micelles formed by PEO−PPO−PEO block copolymers in water.[33−37]

In addition to the form factor that describes the intramicelle structure as discussed above, the structure factor must be accounted for in order to describe intermicellar interactions. Interactions between the micelles are manifested in a correlation peak that appears in the low q range of the neutron scattering patterns generated from the 5 wt % siloxane copolymer solutions (Figure 1). To describe such intermicellar interactions, we utilized the structure factor, S(q), for hard spheres, that has been described in detail in several publications.[19,32−34,37] Representative fits of the core−corona form factor and hard sphere structure factor model to SANS patterns in the range $q = 0.01-0.1$ Å^{-1} are shown in Figure 2. In Figure 2, the intensity is plotted in a linear scale to focus on the q range below 0.05 Å^{-1}. When the intensity is plotted on a log scale, then the range above 0.05 Å^{-1} is better observed, and it can be seen that the model we used can capture the shoulder observed at $q \sim 0.1$ Å^{-1} in Figure 1 where log(intensity) is plotted.

At conditions of high temperature, and for certain mixed solvents, the form factor for monodisperse core−corona sphere described above can no longer fit well the scattering data. The form factor for another shape, i.e., ellipsoid, has been used to fit the data at these conditions. In fitting the ellipsoid form factor, we consider the micelle to be composed of a “dry” ellipsoid core with low SLD (containing mainly siloxane plus PPO) that is surrounded by a homogeneous solution of high SLD (mainly deuterated solvent with some PEO), and the structure factor is to equal 1. The ellipsoid form factor is given by the following expression:[28]

$$P(q) = \int_0^1 \left[\frac{(\sin(z) - z\cos(z))}{z^3}\right] \mathrm{d}x; \qquad z = qR_b\left[1 + x^2\left(\left(\frac{R_a}{R_b}\right)^2 - 1\right)^{1/2}\right] \quad (4)$$

where R_a is the dimension of the semimajor axis and R_b is that of the semiminor axis. Note that, under some conditions, a form factor model of polydisperse spheres provides equally good fit to the SANS data as a form factor model of monodisperse ellipsoids.[28] However, for the system under consideration here, we see no physical basis for an increase in micelle polydispersity

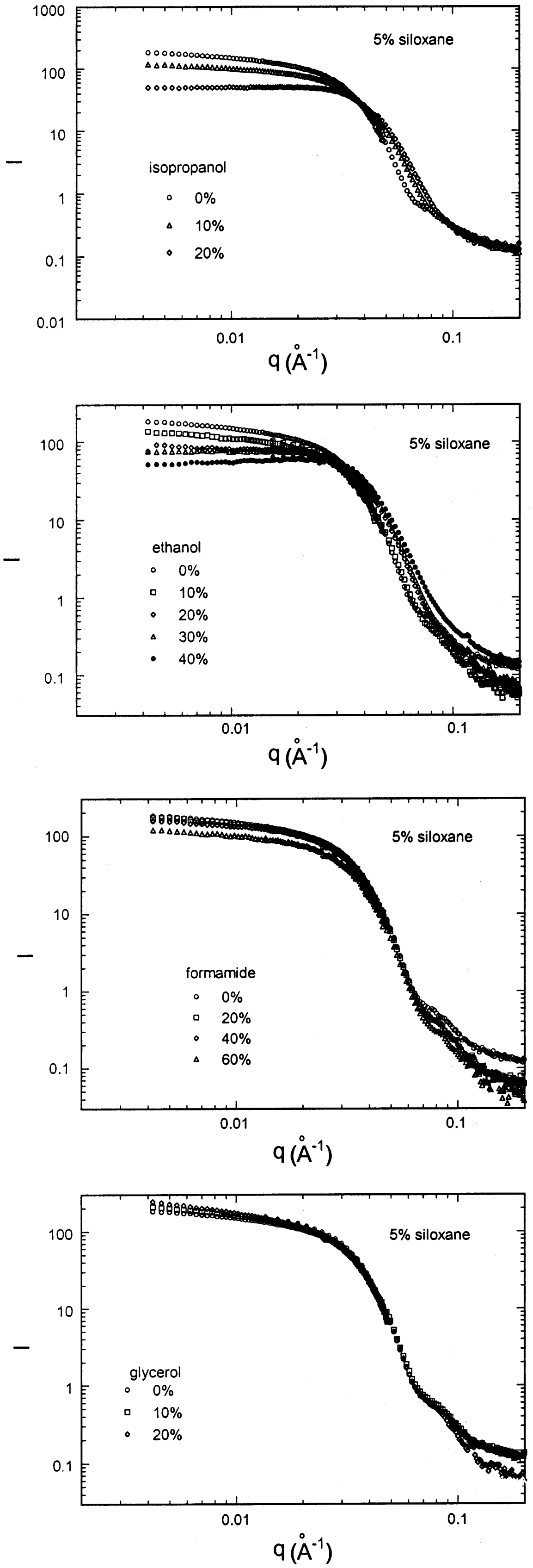

Figure 1. SANS scattering patterns obtained from 5 wt % siloxane copolymer solutions in mixtures of water with different polar organic solvents at various cosolvent contents (the type and concentration of the polar organic solvent is indicated in each graph). The addition of 2-propanol, ethanol, or formamide causes an intensity decrease at low *q*; on the contrary, the addition of glycerol leads to an increase in the scattering intensity at low *q*.

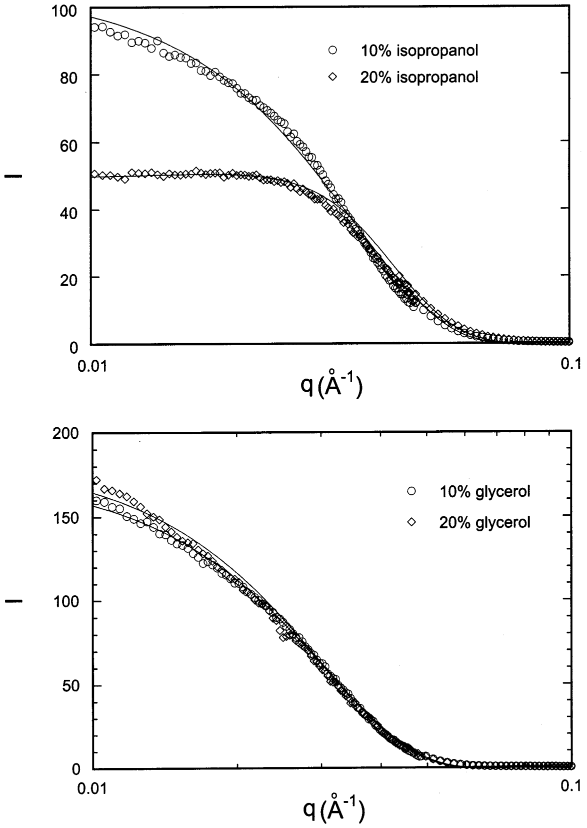

Figure 2. Representative examples of fits of the monodisperse core–corona form factor and hard sphere structure factor model to the SANS scattering intensities, used to extract information of the micelle core and micelle radii and the micelle association number (N_{assoc}). Data are shown for 5 wt % siloxane copolymer in 2-propanol–water and in glycerol–water mixed solvents at 10 and 20 vol % organic solvent contents at 20 °C.

with temperature; after all, micelle formation in aqueous solutions is typically entropy driven and is promoted by an increase in temperature.[29] But we do see a physical basis for a sphere-to-cylinder transition when the PEO segments forming the corona become desolvated[38] due to an increase in the temperature (the inverse temperature solubility of PEO in water is well documented[29]) and/or due to the presence of a specific cosolvent (this is discussed later in the paper). For these reasons, we set aside the issue of polydispersity and focused instead on the shape of the micelles as reflected in the form factor.

Results and Discussion

SANS Patterns Obtained from Siloxane Copolymers at Various Mixed Solvent Conditions. The siloxane copolymer concentration examined here is 5 wt %, which is well above the CMC in the various mixed solvents.[26] When the solvent is deuterated, the presence of micelles causes a strong scattering of neutrons due to the contrast between the solvent-poor micelle core (low SLD) and the solvent-rich corona (intermediate SLD), or/and the solvent phase (high SLD), as well as from intermicellar interactions that give rise to a correlation peak. The evolution of the scattering patterns as a function of the polar organic solvent content in different mixed solvents is shown in Figure 1. The scattering intensity and the shape of the scattering pattern change with an increase of the cosolvent concentration, reflecting a change of the micelle structure. The scattering intensities exhibit a decrease with increasing cosolvent concentration at $q < 0.03$ Å^{-1} for water mixed with ethanol, 2-propanol,

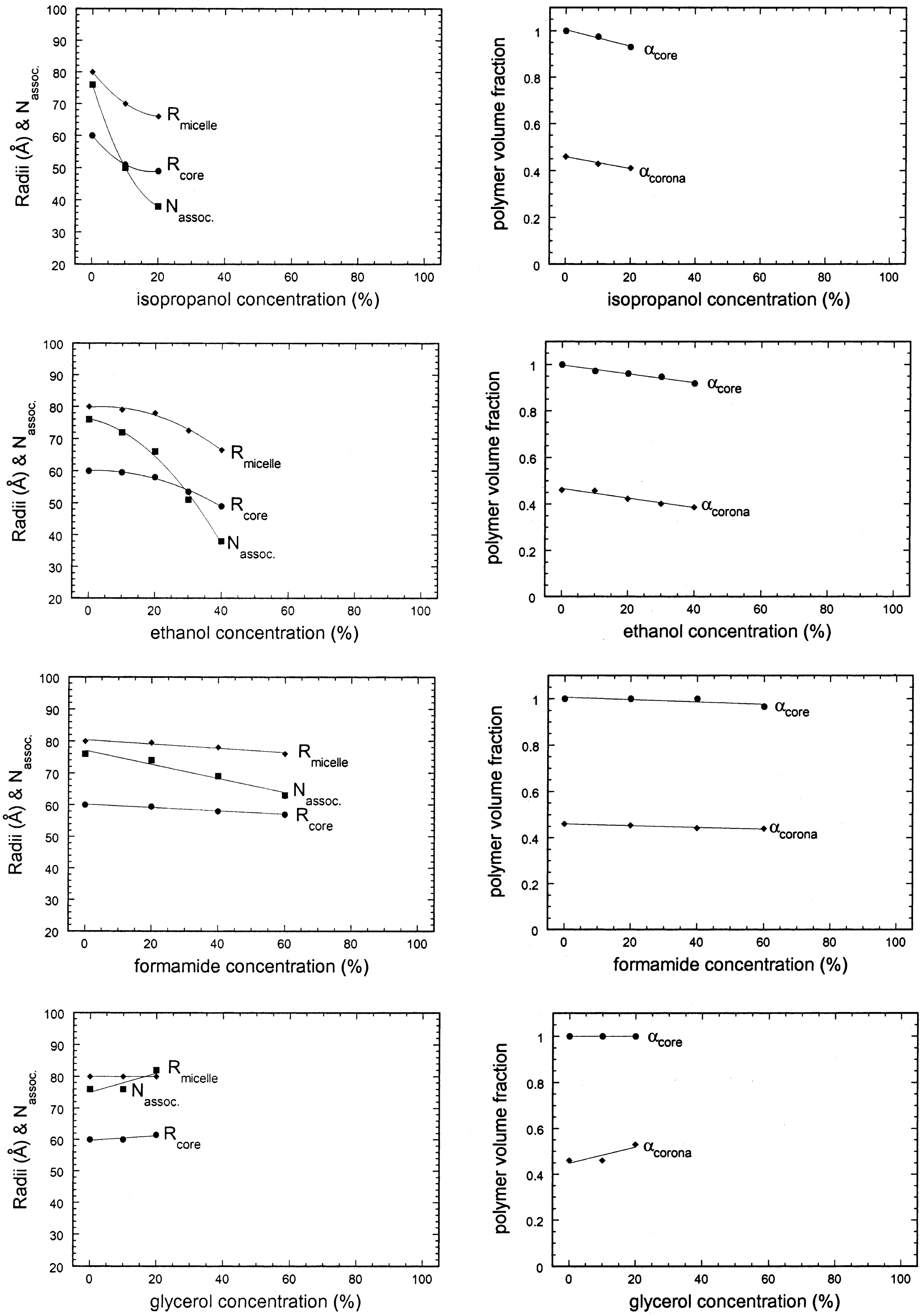

Figure 3. Structural information obtained from SANS in 5 wt % siloxane copolymer solution at 20 °C, plotted as a function of the polar organic solvent content in the mixed solvent. The micelle core radii, micelle radii, micelle association number, and polymer volume fraction in the micelle core and corona decrease with added organic solvent in the water−2-propanol, water−ethanol, and water−formamide mixed solvents. In water-glycerol mixed solvents, the micelle core radii, micelle association number, and polymer volume fraction in the corona increase.

or formamide. On the contrary, the addition of glycerol leads to an increase in the scattering intensity. A side peak ("shoulder") that is observed in some scattering patterns at $q \sim 0.1$ Å^{-1} indicates the formation of dense micelles with sharp interfaces. At these conditions the hard sphere structure factor is taken into account when fitting the scattering intensity data (see Figure 2 for representative fits). While some trends on the effects of cosolvents on the micelle structure can already emerge from a simple inspection of the scattering patterns shown in Figure 1, a quantitative analysis of the scattering patterns (given below) can provide us with detailed information on the structure of the micelles under conditions of various solvent types and compositions, and different temperatures.

Effect of Solvents on the Siloxane Copolymer Micelle Structure. The micelle core and micelle radii (R_{core} and R_{micelle}) and the micelle association number (N_{assoc}) values obtained by fitting the core−corona form factor and hard sphere structure factor (used in some conditions) to the scattering patterns of 5 wt % siloxane copolymer in various mixed solvents at 20 °C are presented in Figure 3; also shown are the volume fraction of polymer in the core (α_{core}) and the volume fraction of polymer in the corona (α_{corona}). Let us first consider the case of plain water as the solvent. The poly(dimethylsiloxane)-graft-polyether copolymer forms in water spherical micelles with a core radius of 60 Å and a micelle radius of 80 Å. This leads to a corona thickness of 20 Å. The relatively thin corona, and its relatively high polymer content (0.4 in the case of the siloxane copolymer considered here, compared to 0.2 in the case of PEO−PPO−PEO block copolymers examined with the core−corona form factor[19,33,34]) are most likely reflections of the comblike architecture of the siloxane copolymer with the short PEO side chains. In turn, the thin corona may be the reason for the weak correlation peak observed in the scattering patterns from the siloxane copolymer micellar solutions. At the same copolymer concentration, PEO−PPO−PEO block copolymer micelles exhibit a stronger correlation peak[19] as the hydrated (and extended) PEO chains repel each other.[39]

The addition of 2-propanol, ethanol, or formamide to the aqueous siloxane copolymer solution has very similar effects on the micelle structure: the micelle core radii and the micelle association numbers decrease with increasing cosolvent content. 2-Propanol has a more pronounced impact on the micelle structure than ethanol and formamide; for example, in the 20/80 vol % 2-propanol/water mixed solvent, N_{assoc} is about half than that observed in pure water. This decrease in N_{assoc} is accompanied by a smaller (~15%) decrease of the micelle core and micelle radii. At 40 vol %, ethanol causes a 50% reduction in N_{assoc} compared with the case of pure water, and a 20% decrease in the core and micelle radii. At 60 vol % formamide, the micelle association number is about 20% smaller than that in plain water, and the radii of the micelle core and micelle are close to those in plain water.

The polymer volume fraction values in the core and corona can shed light on the effects of 2-propanol, ethanol, and formamide on the micelle structure. At 20 vol % 2-propanol in the mixed solvent, the polymer volume fraction in the core (α_{core}) decreases from 1 (i.e., dry micelle core) in pure water to 0.93, and the polymer volume fraction in the corona (α_{corona}) decreases from 0.46 in pure water to 0.41. At 20 vol % ethanol, α_{core} decreases from 1 to 0.96 and α_{corona} from 0.46 to 0.42. When the ethanol content increases to 40 vol %, α_{core} decreases to 0.92 (leaving a relatively high 8 vol % solvent content in the micelle core), while R_{corona} becomes 0.39. The addition of formamide also results in a "swelling" (higher degree of solvation than in water) of both the core and corona, but the effect of formamide is smaller than that of ethanol. The decreasing polymer volume fractions in the micelle core and corona with increasing cosolvent content indicate that both siloxane and polyether are solvated to a higher degree in the water−2-propanol and water−ethanol mixtures than in the water−formamide mixed solvents. The presence in water of 2-propanol and ethanol reduces the solvophobicity and increases the solubility of the siloxane parts, and lowers the interfacial tension between the micelle core and the solvent. These effects lead to a micelle size smaller than that in plain water.[38]

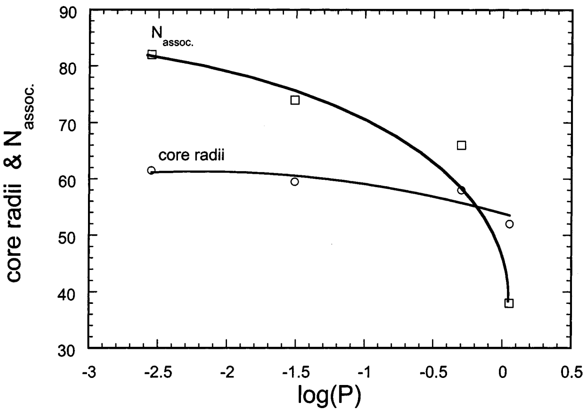

Figure 4. Correlation of the physicochemical characteristics of the polar organic solvents (expressed here in terms of the octanol/water partition coefficient, log(P)) to their effects on the core radius and association number of siloxane copolymer micelles formed in mixtures of 80 vol % water−20 vol % polar organic solvent (at 20 °C). The micelle core radii and association numbers decrease as the log(P) of the solvent increases. The lines drawn are used as a guide to the eye.

Glycerol affects the micelle structure to the opposite direction than ethanol and 2-propanol. As indicated in Figure 3, when the glycerol content increases from 0 to 20 vol %, the micelle association number increases by about 10%; at the same time, the micelle radius remains constant. This is a result of how glycerol affects the presence of solvent in the micelle core and corona. With an increase of glycerol content in the mixed solvent, the polymer volume fraction in the core remains 1, i.e., the micelle core remains "dry". However, the polymer volume fraction in the corona changes from 0.46 in pure water to 0.53 in 20 vol % glycerol. This increase of the polymer volume fraction in the corona suggests that some of the water initially swelling the corona is withdrawn upon the addition of glycerol into water. The addition of glycerol to water has been reported to result in a higher micelle association number and in a decrease in the PEO headgroup hydration also in low molecular weight nonionic ethoxylated surfactants such as $C_{12}EO_8$[27] and in the higher molecular weight Pluronic P105 ($EO_{37}PO_{58}EO_{37}$) block copolymer.[19] The higher association number observed in the presence of glycerol may result from the attempt to reduce the unfavorable interactions between the hydrophobic blocks and the glycerol−water mixed solvent.

The information on the effects of cosolvents on the micelle structure (and in particular on the solvent content in the micelle core and corona) presented above provides indirect evidence on the preference of the polar organic solvents to be located either in the interior (2-propanol and ethanol) or in the exterior (glycerol) of the micelles. To test this "partitioning" hypothesis, we plot in Figure 4 the micelle core radii and association numbers (that have been observed in water mixed with 20 vol % cosolvent) versus the octanol/water partition coefficient (log(P)) of the respective cosolvent. log(P) is a useful parameter

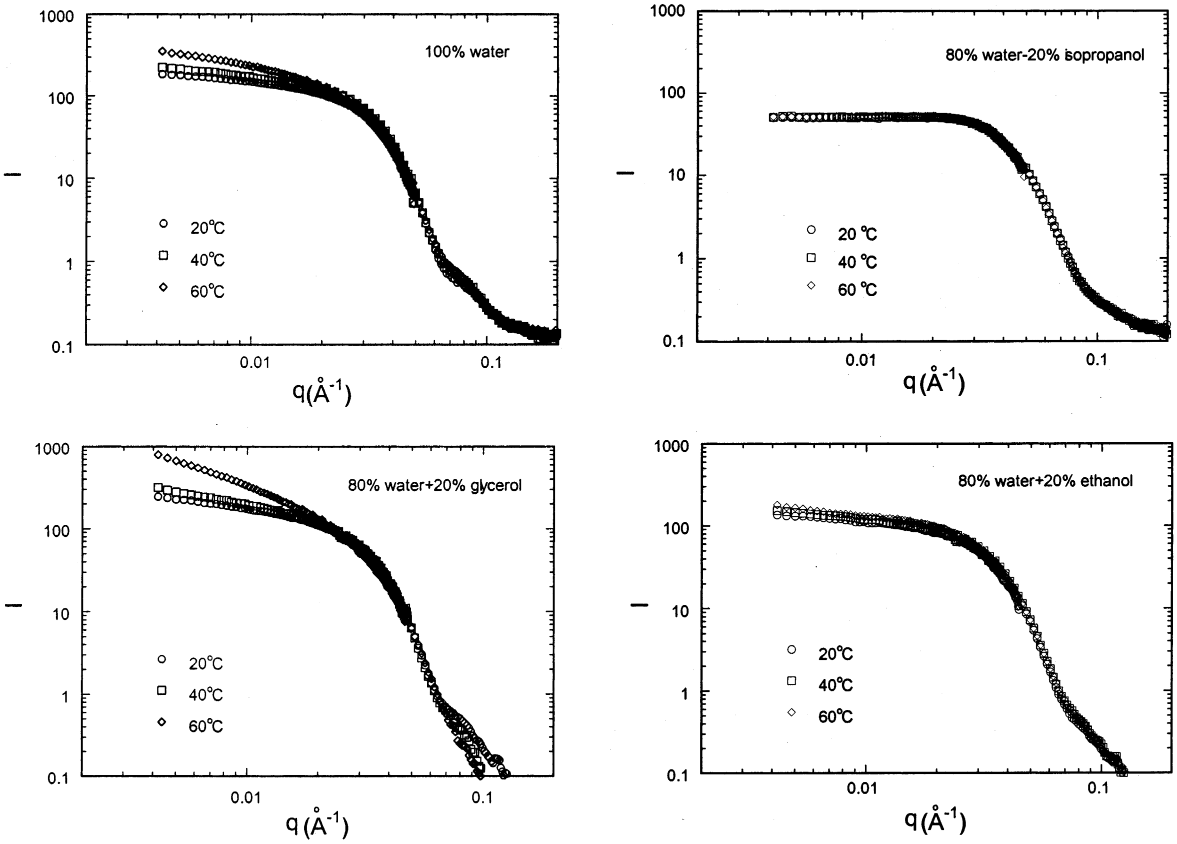

Figure 5. SANS scattering patterns from 5 wt % siloxane copolymer solutions in different solvents shown as a function of temperature in the range 20−60 °C (the temperature values are indicated in each graph). In the mixed solvent cases, the polar organic solvent concentration is 20 vol %. The scattering intensity increases at low q for plain water and for water−glycerol mixed solvent. In water−ethanol and water−2-propanol mixed solvents, the scattering intensity remains almost independent of the temperature.

that can capture physicochemical properties of a given molecule.[19,20] As seen in Figure 4, as log(*P*) increases, the micelle core radius and association number decrease. Note that a negative octanol/water partition coefficient value for a certain molecule indicates that this molecule, given a choice between water and octanol, prefers to partition in water. The log(*P*) value of 2-propanol is 0.05, of ethanol is −0.32 and of formamide is −1.50; thus, these cosolvents are all more hydrophobic than PEO, for which we assume the same log(*P*) value, −1.93, as for ethylene glycol. As a result, the solvent contents in the micelle core and corona increase with increasing amount of 2-propanol, ethanol, or formamide in the mixed solvent. Note that log(*P*) for glycerol is −2.55, which is more negative than that of ethylene glycol (=−1.93) (the compound resembling PEO) and indicates a very strong affinity to water. The decrease of the micelle radius is thus associated with the dehydration of the PEO blocks that counteracts the increase in the micelle association number.

Effect of Temperature on Siloxane Copolymer Micelle Structure. A common way to modulate the solvent quality, other than mixing solvents, is to change the temperature. We therefore examined the temperature effects on the siloxane copolymer micelle structure by SANS. As seen in Figure 5, the scattering intensities obtained for 5 wt % siloxane copolymer at 40 and at 60 °C coincide with the data obtained at 20 °C in the cases of 80/20 vol % water−2-propanol and water−ethanol mixtures. As discussed above, these scattering patterns can be adequately fitted by the core−corona form factor. However, for the cases of plain water and 80/20 vol % water−glycerol mixture, the scattering intensity at low q ($<$0.01 Å^{-1}) increases at 40 °C (compared to that in 20 °C), and increases even further at 60 °C. For these micelles the core−shell form factor no longer fits well the data (as attested by the dashed curve in Figure 6). Because of the lower solvation and higher hydrophobicity of the PEO blocks at the higher temperature, the micelles will tend to grow. Under the restrictions that all the polar PEO segments are exposed to the solvent and there is no space that is not filled with the hydrophobic chains in the micelle core, micelles will grow along one dimension (to form rods), and further to two dimensions (to form disks).[38]

We fitted the data for the siloxane copolymer micelles in plain water and in the 80/20 vol % water−glycerol mixture at 60 °C by the monodisperse ellipsoid form factor (eq 4) with the semimajor axis R_a and semiminor axis R_b (we selected an ellipsoid shape as an intermediate stage between a sphere and a cylinder). As shown in Figure 6, the ellipsoid form factor gives a much better fit than the core−shell form factor for the water−glycerol mixture at low q. The calculated R_a is 160 Å and R_b is 61 Å in plain water, where b is the axis of symmetry. R_a is 450 Å and R_b is 65 Å for the water−glycerol mixture. Note that the semiminor axis R_b has the same value as the (spherical) micelle core radius at 20 °C. This confirms the structural length scale imposed by the siloxane copolymer molecules as the micelles undergo a sphere to cylinder transition. Note also that R_b has a similar value in plain water and in the water-glycerol mixture, whereas R_a increases from 160 Å in plain water to 450 Å in water-glycerol solution. This is the result of a “double-punch” effect, where the dehydrating effect of temperature on PEO is compounded by presence of glycerol (which as discussed in the previous section tends to desolvate the corona of the micelle). Because of the higher hydrophobicity of the PEO chains at 60 °C, the siloxane copolymer micelles

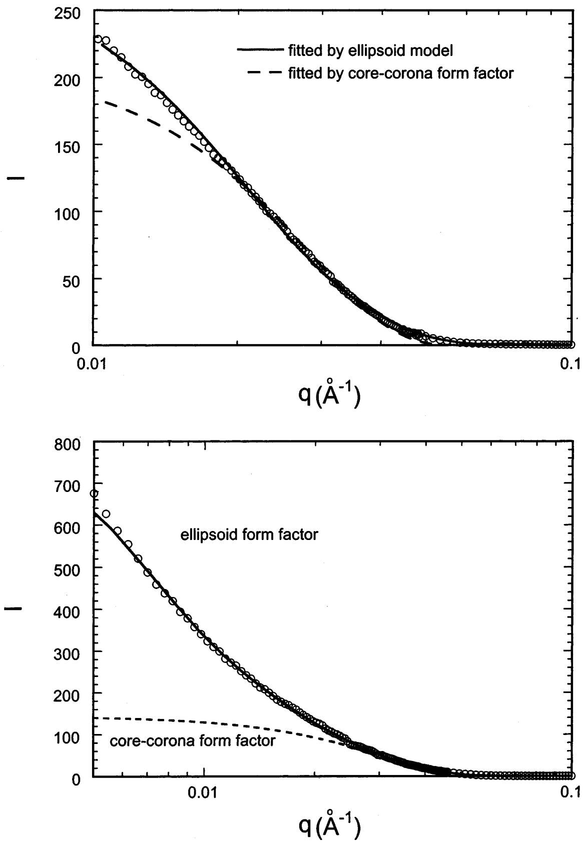

Figure 6. Representative examples of fits of the core−corona form factor model (dashed line) and ellipsoid (solid line) to the SANS scattering intensities. The ellipsoid form factor gives a better fit to the scattering data. Data are shown for 5 wt % siloxane copolymer in plain water (top part) and in water−glycerol mixed solvent (bottom part) at 60 °C. R_a and R_b information can be extracted from the fits and is reported in the text.

tend to increase their size and change their shape in plain water. If we further add glycerol to the solution, we expect to have a longer micelle than in plain water to better reduce the unfavorable contact between the hydrophobic chains and solvents.

Though the PEO chains become more solvophobic at 60 °C, the increase in the scattering intensity in water−ethanol and water−2-propanol mixtures is much smaller compared to that observed in water and water-glycerol solution as shown in Figure 5. As discussed earlier, the effect of 2-propanol and ethanol is to reduce the core radii, micelle radii, and association numbers by means of increasing the solvation of both the polyether and siloxane chains. This cosolvent effect thus counteracts the temperature effect, and the micelles remain spherical.

Micelles formed by siloxane copolymers with structure similar to ours, $MD_nD'_mRM$ (with $R = CH_2-(EO)_{12}-OH$), $n = 13$ or 18, $m = 5$), have been found to fit the spherical models,[7] but the authors suggested that these micelles have ellipsoidal shape with an axial ratio close to 1 and the experimental accuracy is not sufficient to distinguish between such ellipsoids and exact spheres. SANS data on $MD_{13}D'_5M$ with $R = (CH_2)_3EO_{12}OH$ and on $MD_{20}D'_5M$ with $R = (CH_2)_3EO_{10}PO_4OH$, reported very recently in ref 12, were fitted well to a monodisperse oblate ellipsoid model, in good agreement with the observed transition of the micelle structure from spherical to ellipsoid at higher temperature discussed above. The structural dimensions obtained in ref 12 are lower than the ones reported here, which is reasonable given that the siloxane copolymers examined in ref 12 have lower molecular weight than that examined here.

Comparison of Solvent Effects and Temperature Effects. From a comparison of the cosolvent effects with the temperature effects on the siloxane copolymer structure, we can see that the addition to water of 2-propanol or ethanol causes a micelle structure change similar to that caused by a reduction in temperature. The solvent conditions in the micelle core and corona improve with a decrease in temperature or with the addition of 2-propanol, ethanol, or formamide; correspondingly, the radii of the micelle core and micelle, as well as the micelle association numbers, decrease and thus the siloxane copolymer molecules form spherical micelles. On the contrary, the addition of glycerol into water leads to a micelle structure change comparable to that caused by an increase of temperature: upon addition of glycerol, the solvent conditions in the micelle corona become worse, the micelle association number increases, the micelles grow and become ellipsoids, trends which are also observed in plain water with an increase of the temperature. It should be noted that a temperature increase from 20 to 60 °C results in a stronger effect on the formation of ellipsoid micelles in plain water than the addition of 20% glycerol at 20 °C as judged by the scattering patterns. 20% ethanol or 2-propanol present in solution at 60 °C have stronger effects in reducing the micelle size than in 20 °C. From the above it becomes evident that temperature and cosolvents can act in tandem or in opposition. Such information is very useful in waterborne formulations.

Conclusions

The effects of polar organic solvents such as 2-propanol, ethanol, formamide and glycerol on the structure of micelles formed in water by an amphiphilic poly(dimethylsiloxane)-graft-polyether copolymer have been investigated as a function of the cosolvent content in the mixed solvent and the solution temperature using SANS. Such fundamental information on cosolvent and temperature effects on the solution structure of polymeric amphiphiles is beneficial in the context of the increased use of functional polymers in a variety of products, e.g., pharmaceutics, personal care products, detergents, coatings, and inks.

A core−corona form factor was used to extract information about the micelle size (R_{core} and $R_{micelle}$) and micelle association number (N_{assoc}). The polymer volume fractions in the core and the corona (α_{core} and α_{corona}) were calculated on the basis of the above fitting parameters. The siloxane copolymer forms in water at 20 °C micelles that consist of a “dry” core with a radius of about 6 nm and a solvated (about 40% polymer) corona with a thickness of 2 nm; the relatively thin corona may be due to the comb-type architecture of the siloxane copolymer. The addition of 2-propanol, ethanol, or formamide into water has similar effects on the micelle structure, but the effect of 2-propanol is more pronounced. The micelle core and micelle radii and the micelle association number decrease progressively upon the addition of 2-propanol or ethanol, accompanying a decrease of the polymer volume fraction in the micelle core and corona. These cosolvents offer better solvent condition for this siloxane copolymer and lead to higher solvation of siloxane and polyether segments than water. The addition of glycerol, however, increases the micelle association number. At the same time, the polymer volume fraction in the micelle corona increases when the glycerol content increases from 0 to 20 vol %.

Judging from their octanol/water partition coefficients, log(*P*), 2-propanol, ethanol, and formamide, although all completely miscible with water, are hydrophobic compared with the PEO, and they have a higher affinity than water for the hydrophobic siloxane blocks. Glycerol has the most negative log(*P*) among the cosolvents examined here. In the presence of glycerol, the amount of water hydrating the polyether corona decreases.

An increase of temperature from 20 to 60 °C results in a transition from spherical to ellipsoid micelles as revealed by the increase in the scattering intensity at low *q* values. Because water at high-temperature becomes worse solvent for the siloxane copolymer, larger micelles tend to form in order to reduce contact between hydrophobic segments and the solvent. The addition of glycerol compounds the dehydrating effect of temperature and therefore longer ellipsoids are formed. The presence in water of 2-propanol or ethanol can counteract the temperature effect, and the micelles remain spherical.

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