Macromolecules **2000,** *33,* 5574−5587

SANS Investigation of Polyether Block Copolymer Micelle Structure in Mixed Solvents of Water and Formamide, Ethanol, or Glycerol

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Received February 23, 2000; Revised Manuscript Received May 2, 2000

ABSTRACT: The solution structure of a representative polyether block copolymer (Pluronic P105: EO_{37}-$PO_{58}EO_{37}$, where EO and PO denote ethylene oxide and propylene oxide segments, respectively) has been investigated in mixed solvents (selective for the PEO block) consisting of water and one of the following polar cosolvents: formamide, ethanol, and glycerol. $EO_{37}PO_{58}EO_{37}$ self-assembles to form micelles in all the cosolvent−water mixed solvents examined, above a certain concentration (cmc) and temperature (cmt) which depend on the cosolvent type and content. Micelle structural parameters were obtained as a function of the cosolvent−water ratio, solution temperature, and block copolymer concentration by fitting a core−corona form factor and a hard-sphere interaction structure factor to small-angle neutron scattering (SANS) data. 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 formamide or ethanol. Addition of glycerol led to higher micelle association number and higher polymer volume fraction in the micelle corona. The above findings are discussed in terms of the solvent quality in the mixed solvents. An increase in temperature resulted in higher micelle association number and a lower degree of solvation in the micelle core and corona in all the cosolvent−water mixed solvents examined.

Introduction

The interest in the nature of self-assembly of amphiphiles in solvents less polar than water or in mixtures of such solvents with water is driven by both fundamental and practical considerations.[1] For example, cosolvents (such as glycerol and ethanol) and simple salts are often present in drug delivery formulations that employ amphiphiles as excipients or carriers.[2] In such pharmaceutical formulations, the cosolvents are added in order to improve the solubility of the active compounds and/or to aid in the sensory perception (e.g., viscosity, sweetness), while salts usually act as buffers. Nonaqueous polar solvents are also present in water-based inks used in ink-jet printers.[3] Here, water is the primary solvent because of its thermal properties (water evaporation is used to eject the ink drops from the printer head), but cosolvents are needed in order to modulate the ink−paper interactions. A number of reports have appeared on the micellization of low-molecular-weight surfactants in solvents less polar than water, such as mixtures of water with formamide, glycerol, or ethylene glycol.[1,4−8] Our research interest is on macromolecular amphiphiles and, in particular, on polyether block copolymers such as poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO−PPO−PEO), commercially available as Poloxamers or Pluronics.[9] PEO−PPO−PEO block copolymers find numerous applications[10−12] on the basis of their ability to self-assemble in aqueous solution and to modify interfacial properties.[13,14]

Block copolymers dissolved in selective solvents can associate to form micelles, with the solvent-insoluble polymer block forming the micelle core and the solvent-soluble block the corona.[15,16] The solvent quality is a controlling factor in the self-assembly and microstructure of block copolymers.[16] In the case of PEO−PPO−PEO block copolymers where water is typically used as a solvent (being selective for PEO), the addition to water of cosolutes,[17,18] such as urea and common salts, or cosolvents,[19−23] such as glycerol, ethanol, and formamide, provides extra degrees of freedom in tailoring the solution properties for specific applications.[14,16] The addition of cosolvents also causes pronounced effects on the concentration range of stability of the different lyotropic liquid crystals formed by PEO−PPO−PEO block copolymers in water and on the characteristic length scales of the microstructures.[23−25] However, the published information on the effects of cosolvents on the solution behavior of polymeric amphiphiles (e.g., water-soluble block or graft copolymers) is rather 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. Further study is required in order to obtain detailed information on the cosolvent location in the microstructure and the solvation of the hydrophobic PPO and hydrophilic PEO segments when cosolvents are present in aqueous PEO−PPO−PEO solutions.

We address here the structure of a representative polyether (PEO−PPO−PEO) block copolymer in mixed solvents consisting of water and one of the following cosolvents: formamide, ethanol, or glycerol. The principal means of characterization is small-angle neutron scattering (SANS).[26] SANS has been used extensively in the structural characterization of aqueous PEO−PPO−PEO block copolymer solutions.[27−31] We employed SANS to examine the concentration−temperature conditions under which micelles form and to obtain (by fitting to an appropriate model for the form and

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10.1021/ma000332o CCC: $19.00 © 2000 American Chemical Society
Published on Web 07/07/2000

structure factor) micelle structural parameters such as radius, association number, and polymer volume fraction in the micelle core and corona. We thus provide a comprehensive picture of how the presence of cosolvents affects the self-assembly of polyether block copolymers.

Materials and Methods

Materials. The Pluronic P105 poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer was obtained from BASF Corp. and was used as received. Pluronic P105 is denoted here as $EO_{37}PO_{58}EO_{37}$ on the basis of its nominal molecular weight of 6500 and 50% PEO content. Deuterated water (D_2O), deuterated formamide ($DCOND_2$), deuterated ethanol (CD_3CD_2OD), and deuterated glycerol ($CD_2ODCDODCD_2OD$) were purchased from Cambridge Isotope Laboratories. Care was taken to avoid exposure of the cosolvents to atmospheric humidity.

Small-Angle Neutron Scattering (SANS). SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR), beam guide NG3. The sample-to-detector distance was 260.0 cm. The resolution ($\Delta q/q$) was about 0.15. The angular distribution of the scattered neutrons was recorded in a two-dimensional detector. For a given scattering vector value, q^*, the scattering intensity was obtained by averaging the intensity of all the points on the 2-D detector space whose distance from the central point is q^*. This circular average scattering intensity was used for data analysis. Scattering intensities from the block copolymer solutions were corrected for detector background, empty cell scattering, and sample transmission. The $EO_{37}PO_{58}EO_{37}$ solutions (concentration: 1 and 8 wt %) were placed in stoppered 1 mm path length "banjo" quartz cells. The compositions of the cosolvent−water mixed solvent examined here were 0, 20, 40, 60, 80, and 100 vol % formamide; 0, 5, 10, 20, and 40 vol % ethanol; and 0, 10, and 20 vol % glycerol. Scattering data were recorded at different temperatures in the range 10−60 °C. More than 45 min was allotted for thermal and kinetic equilibration.[32]

SANS Data Analysis: Unimer Structure. At low temperatures and concentrations, the block copolymers are present in solution as independent polymer chains (unimers). Within the experimental error, the scattering function of these unimers is in agreement with that of polymers obeying a Gaussian conformation (Debye function for the form factor of random coils, F_{coil}):[33,34]

$$F_{\text{coil}}(q) \sim x^{-2}[\exp(-x) + x - 1] \qquad (1)$$

where $x = (qR_g)^2$, and R_g is the polymer chain radius of gyration. The unimer radius of gyration (R_g) is obtained from the best fit of eq 1 to the SANS scattering data (as seen in Figure 1).

SANS Data Analysis: Micelle Structure. Upon a temperature increase, the solvent conditions become progressively worse and the $EO_{37}PO_{58}EO_{37}$ unimers self-assemble into micelles. It is well accepted that the PEO−PPO−PEO micelles are composed of a core dominated by the hydrophobic PPO blocks and surrounded by a corona of solvated hydrophilic PEO blocks. This unique core−corona structure can be explored by SANS due to the uneven distribution of deuterated solvent in the solvent phase, solvated PEO corona, and the relatively "dry" PPO core. If we consider the micellar solution to be a monodisperse system, then the SANS scattering intensity can be expressed as a product of the form factor, $F(q)$, and the structure factor, $S(q)$, as shown in eq 2, where $\Delta\rho$ is the scattering length density contrast between the micelle particles and the solvent, and N is the micelle number density. The form factor describes the structure of the micelle particle, while the structure factor describes the interaction between the micelle particles.[33,34]

$$I(q) = (\Delta\rho)^2 N F(q)\, S(q) \qquad (2)$$

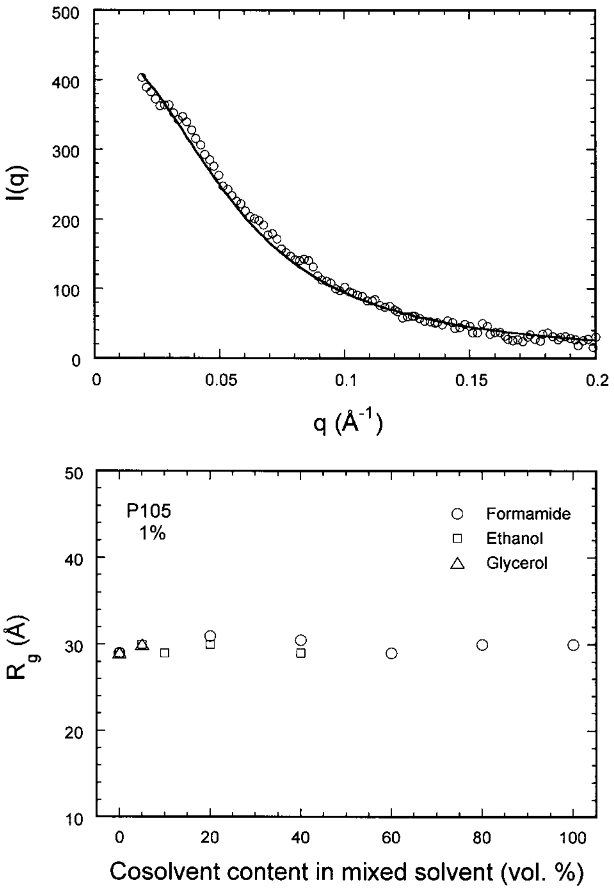

Figure 1. (top) Representative example of the best fit (solid line) of the Debye function to SANS scattering intensity data (empty circles) obtained from a 1 wt % $EO_{37}PO_{58}EO_{37}$ solution in formamide/water mixed solvent with 60 vol % formamide content at 10 °C. (bottom) Radius of gyration of $EO_{37}PO_{58}EO_{37}$ (1 wt %) unimers in formamide−water, ethanol−water, and glycerol−water mixed solvents at 10 °C plotted as a function of the cosolvent vol % content. The error bar is smaller than the size of the symbols denoting the data points.

A core−corona form factor has been proposed to describe the scattering generated from the contrast between the micelle core and corona, which have different solvent contents (the core is usually "dry" or has small amounts of solvent, whereas the corona is highly solvated), and the scattering due to the contrast between the micelle corona and the solvent phase:[22,29]

$$F(q)(\Delta\rho)^2 = \{(4\pi R_{\text{core}}^{\ 3}/3)(\rho_{\text{core}} - \rho_{\text{corona}})[3J_1(qR_{\text{core}})/(qR_{\text{core}})] + (4\pi R_{\text{micelle}}^{\ 3}/3)(\rho_{\text{corona}} - \rho_{\text{solvent}})[3J_1(qR_{\text{micelle}})/(qR_{\text{micelle}})]\}^2 \qquad (3)$$

where R_{core} and R_{micelle} are the radii of the micelle core and whole micelle (core + corona), respectively (see Figure 2 for a schematic of the block copolymer micelle core−corona structure); 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:

$$J_1(y) = [\sin(y) - y\cos(y)]/y^2 \qquad (4)$$

Under the assumption that only PPO (and all the PPO) is present in the core and only PEO (and not PPO) is present in corona (solvent is also present in the micelle core and corona), the SLD of the core, ρ_{core}, and the corona, ρ_{corona}, are a function of the average (over the core radius) volume fraction of PPO in the core (α_{core}) and of the average volume fraction of PEO

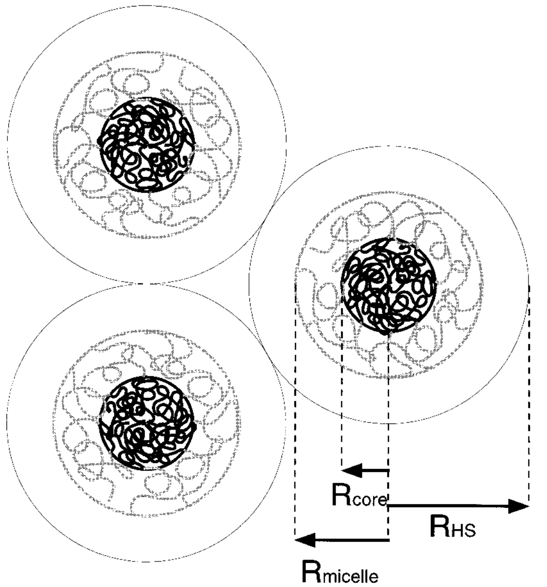

Figure 2. Schematic of block copolymer micelles. R_{core} and $R_{micelle}$ are the radii of the micelle core and core + corona, respectively. R_{HS} is the hard-sphere interaction distance. When the micelle concentration is relatively low, micelles are well separated and $R_{HS} > R_{micelle}$. When the micelle concentration is high, $R_{HS} \approx R_{micelle}$.

in the corona (α_{corona}), respectively:

$$\rho_{core} = \alpha_{core}\rho_{PPO} + (1 - \alpha_{core})\rho_{solvent}$$
$$\rho_{corona} = \alpha_{corona}\rho_{PEO} + (1 - \alpha_{corona})\rho_{solvent} \quad (5)$$

where ρ_{PPO} (=0.325 × 10^{10} cm^{-2}) and ρ_{PEO} (=0.547 × 10^{10} cm^{-2}) are the SLD of PPO and PEO, and $\rho_{solvent}$ is the SLD of the water–cosolvent mixture ($\rho_{D-formamide} = 6.38 \times 10^{10}$ cm^{-2}, $\rho_{D-ethanol} = 6.18 \times 10^{10}$ cm^{-2}, $\rho_{D-glycerol} = 7.58 \times 10^{10}$ cm^{-2}, and $\rho_{D_2O} = 6.48 \times 10^{10}$ cm^{-2}).[26] The volume fraction of PPO in the core (α_{core}) and the volume fraction of PEO in the corona (α_{corona}) can be expressed in terms of the core and micelle (core + corona) radii (R_{core} and $R_{micelle}$) and the micelle association number, $N_{association}$, i.e., the number of block copolymer molecules which (on the average) participate in one micelle:

$$\alpha_{core} = 3N_{association}V_{PPO}/(4\pi R_{core}^{3})$$
$$\alpha_{corona} = 3N_{association}V_{PEO}/[4\pi(R_{micelle}^{3} - R_{core}^{3})] \quad (6)$$

where V_{PPO} is the volume of the PPO block (V_{PPO} = 5530 Å^3) and V_{PEO} is the volume of the PEO blocks (V_{PEO} = 5410 Å^3) of one $EO_{37}PO_{58}EO_{37}$ molecule.

In summary, there are three fitting parameters in the core–corona form factor: the core and micelle radii, R_{core} and $R_{micelle}$, and the micelle association number, $N_{association}$. The volume fraction of polymer in the core and corona can be calculated on the basis of these three fitting parameters, according to eq 6. A core–corona form factor which accounts explicitly for the solvent content in the micelle core and corona is very useful in the case of PEO–PPO–PEO block copolymer micelles which undergo a progressive solvent loss in both the corona and the core when the temperature increases.[29] The cosolvent effects can also be probed with such a form factor.[22]

In addition to the form factor described above, the structure factor must be accounted for in order to describe intermicellar interactions. Strong interactions between the micelles are manifested in the correlation peak that becomes evident in the low q range of the neutron scattering patterns generated from the 8 wt % block copolymer solutions (see Figure 3). To describe such intermicellar interactions, we utilized the structure factor, $S(q)$, applicable for hard spheres:[33]

$$S(q) = 1/[1 + 24\Phi G(2qR_{HS})/(2qR_{HS})] \quad (7)$$

Φ is the micellar volume fraction, and R_{HS} is the hard-sphere interaction distance (see Figure 2).

$$G(A,\Phi) = \alpha(\sin A - A\cos A)/A^2 + \beta(2A\sin A + (2 - A^2)\cos A - 2)/A^3 + \gamma\{-A^4\cos A + 4[(3A^2 - 6)\cos A + (A^3 - 6A)\sin A + 6]\}/A^5 \quad (8)$$

where α, β, and γ are

$$\alpha = (1 + 2\Phi)^2/(1 - \Phi)^4$$
$$\beta = -6\Phi(1 + \Phi/2)^2/(1 - \Phi)^4$$
$$\gamma = (\Phi/2)(1 + 2\Phi)^2/(1 - \Phi)^4$$

Φ is a function of the block copolymer concentration (C) and the polymer volume fraction in the core (α_{core}) and corona (α_{corona}), which in turn are a function of the fitting parameters R_{core}, $R_{micelle}$, and $N_{association}$ obtained from the core–corona form factor (as shown in eq 6):

$$\Phi = C(V_{PPO}/\alpha_{core} + V_{PEO}/\alpha_{corona})/(V_{PPO} + V_{PEO}) \quad (9)$$

In this study, we fitted the scattering pattern with the core–corona form factor (eqs 3–6) and the structure factor described in eqs 7–9. The micelle core and core + corona radii (R_{core} and $R_{micelle}$), micelle association number ($N_{association}$), and the hard-sphere interaction distance (R_{HS}) were obtained as the fitting parameters. The solvation conditions in both core and corona were reflected in the volume fraction of PPO in the core (α_{core}) and of PEO in the corona (α_{corona}), calculated by eq 6. Representative fittings are shown in Figure 3.

In the above calculations of the core and corona SLD (ρ_{core} and ρ_{corona}) and of the polymer volume fraction in the core and corona (α_{core} and α_{corona}), we assumed a sharp boundary between the micelle core and corona. We also assumed that PPO blocks are present only in the core and PEO blocks only in the corona. These assumptions may seem severe since it is possible that PPO and PEO mix to a certain extend at the core–corona boundary. However, the calculation of the polymer volume fraction in the core and corona will still be valid even if there is some PEO in the core and some PPO in the corona, as long as the amount of PPO present in the corona is comparable to the amount of PEO present in the core. Note that the SLD of PPO and of PEO are very close to each other compared with the SLD of the deuterated solvents, as shown in Figure 4. Therefore, the calculation of the SLD of the core and corona will have very little change even if PEO and PPO were mixed at the core–corona boundary. We also assumed that the cosolvent mixes evenly with water throughout the solution. This may not be the case owing to the different affinity of the cosolvent to the hydrophobic PPO and hydrophilic PEO blocks.[24,25] However, as indicated by Figure 4, the SLD of D-formamide and D-ethanol are very similar to that of D_2O, and we cannot experimentally distinguish the location of these deuterated solvents. The SLD of D-glycerol is about 15% higher than that of the D_2O. Still, in the analysis of the effects of glycerol on the micelle structure, we used the results obtained from a 8 wt % $EO_{37}PO_{58}EO_{37}$ solution with the relatively low (10 vol %) glycerol content. Therefore, the possibly uneven distribution of the cosolvent and water should not affect the results of the SANS fittings presented in this work.

Results and Discussion

SANS Patterns Obtained from PEO–PPO–PEO Block Copolymers at Various Mixed Solvent Conditions. The evolution of the scattering patterns as a

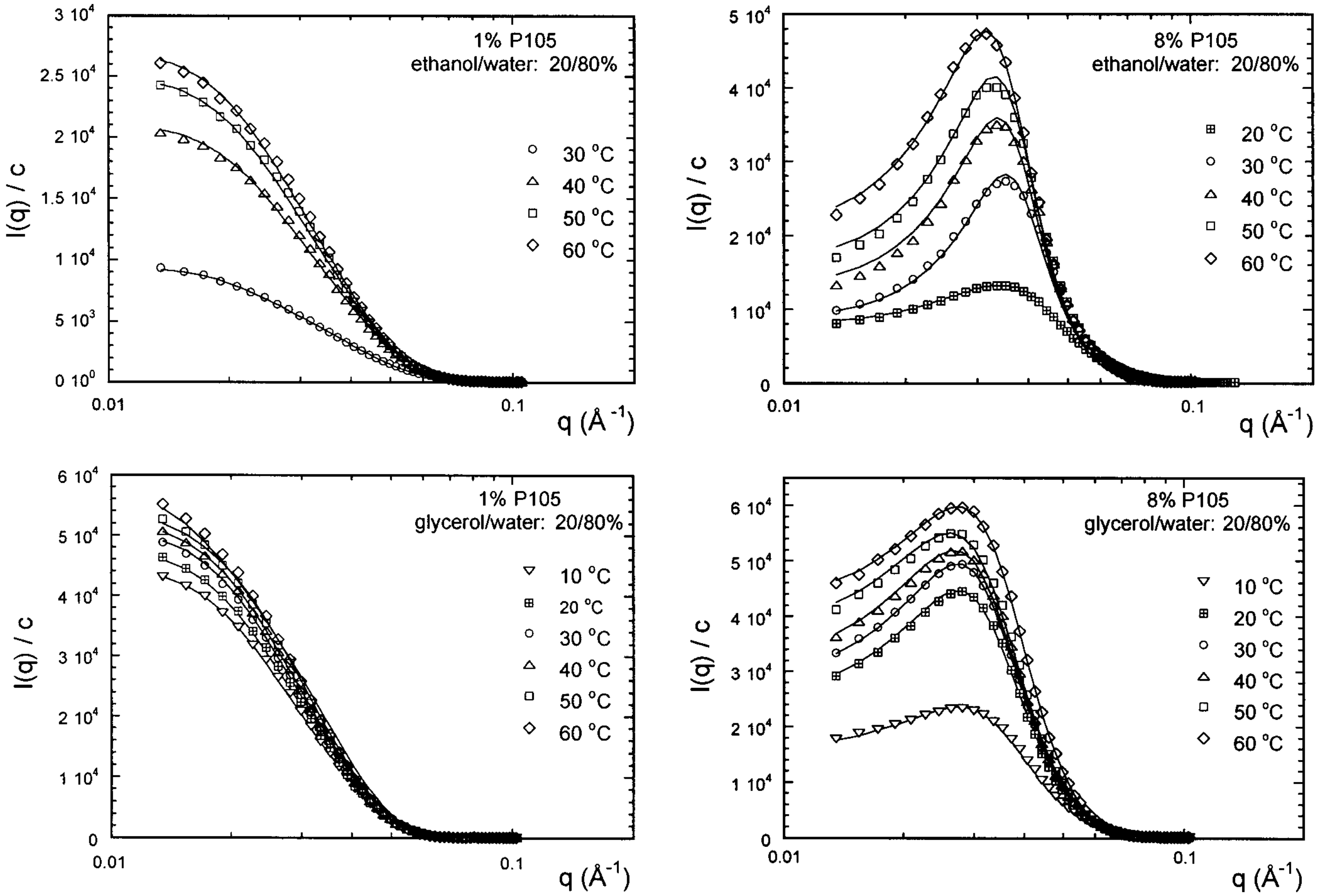

Figure 3. Representative examples of fits of the core–corona model (discussed in the text) to the SANS scattering intensities, used to extract information on the micelle core and core + corona radii (R_{core} and $R_{micelle}$), hard-sphere interaction distance (R_{HS}), and micelle association number ($N_{association}$). Data are shown for (left column) 1 wt % and (right column) 8 wt % $EO_{37}PO_{58}EO_{37}$, in ethanol–water mixed solvent with 20 vol % ethanol, (top row) and in glycerol–water mixed solvent with 20 vol % glycerol (bottom row), in the temperature range 30–60 °C.

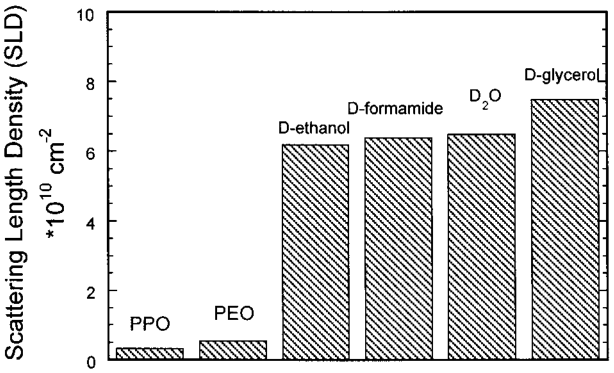

Figure 4. Comparison between the scattering length densities (SLD) of the hydrogenated PEO and PPO blocks and those of the deuterated solvents: D_2O, D-formamide ($DCOND_2$), D-ethanol (CD_3CD_2OD), and D-glycerol ($CD_2ODCDODCD_2OD$).

function of temperature (over the 10–60 °C range) for $EO_{37}PO_{58}EO_{37}$ block copolymer (concentration 1 and 8 wt %) in pure water and in cosolvent/water mixed solvents is shown in Figure 5. The scattering intensity and the shape of the scattering pattern change with an increase of the temperature, reflecting the evolution of the solution structure. At low temperatures (10 °C), the scattering intensity is low, and the scattering function shows a weak *q* dependence, which originates from unimers. At higher temperatures, the scattering intensity increases dramatically and becomes increasingly dominated by a correlation peak at low (<0.1 Å^{-1}) *q* values, resulting from the association of unimers into micelles having well-defined shape and strong intermicellar interactions. A side maximum peak observed in some scattering patterns indicates the formation of dense spherical micelle with sharp interfaces.[33]

As seen in Figure 5, at high (>0.1 Å^{-1}) *q* values the scattering intensity does not vary much at low temperatures (where unimers exist) and at higher temperatures (where micelles are supposed to form). The scattering at such high *q* values originates from polymer chains obeying a Gaussian conformation. Therefore, the superficial similarity of the scattering intensity at $q >$ 0.1 Å^{-1} in a temperature range which spans the unimer and micelle range reflects the presence of solvated PEO segments and of polymer dissolved in the solvent domains even when well-defined micelles are prevalent. A closer look reveals a slight decrease of the scattering intensity with increasing temperature at a fixed block copolymer concentration, suggesting that the concentration of such Gaussian chains decreases as the unimer-to-micelle equilibrium is shifted to favor micelles.

A close inspection of Figure 5 reveals that the scattering pattern of 8 wt % $EO_{37}PO_{58}EO_{37}$ in 20/80 vol % glycerol/water mixed solvent at low temperature (10 °C) is different from those in other solvents. This scattering pattern is typical of micelles and indicates that, in the presence of glycerol in the aqueous solvent, the unimer-to-micelle transition occurs at lower temperatures than in plain water. We also noticed other differences in the

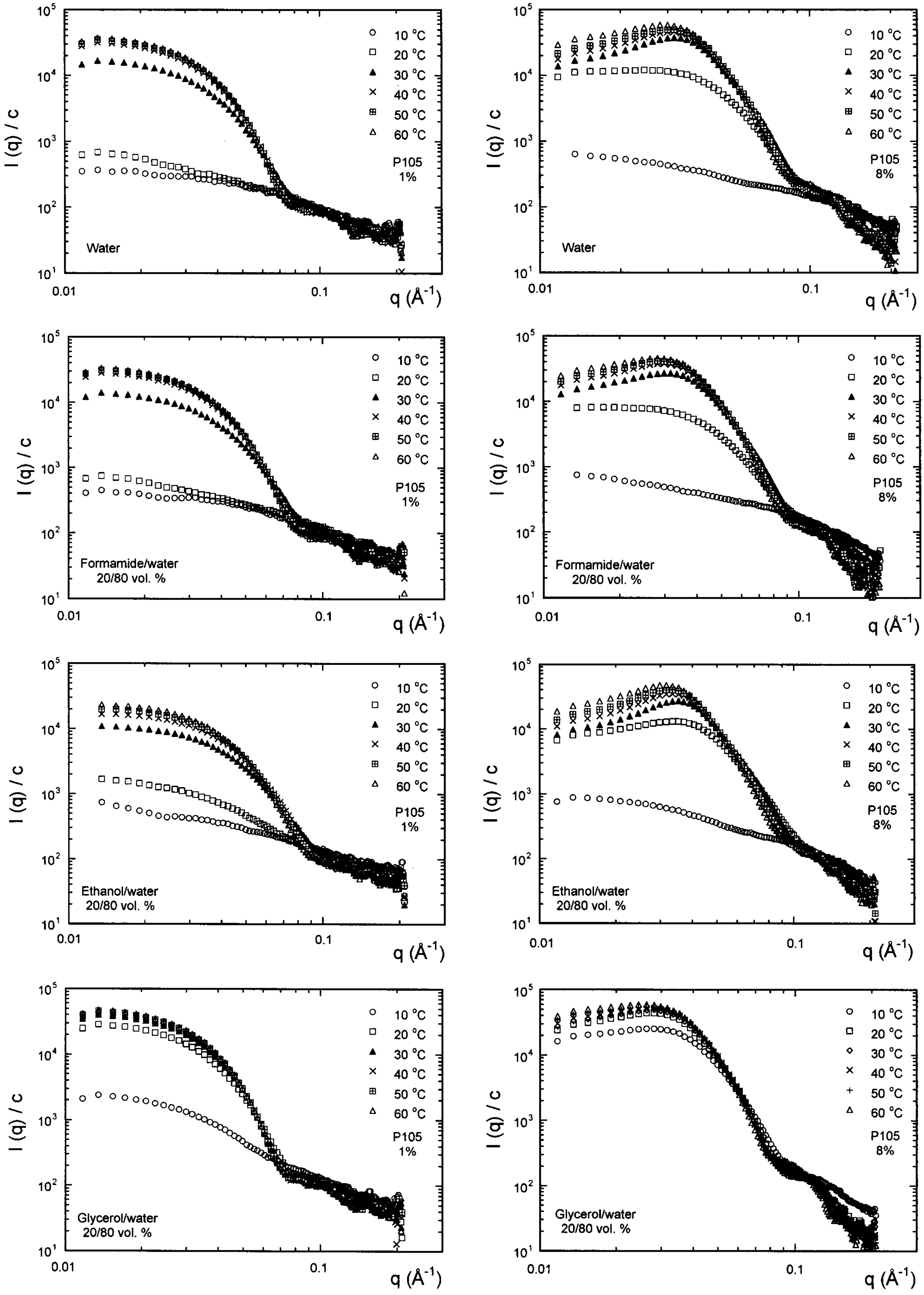

Figure 5. Representative SANS scattering patterns from EO$_{37}$PO$_{58}$EO$_{37}$ solutions in different solvents as a function of temperature (10, 20, 30, 40, 50, 60 °C). The block copolymer concentration is 1 wt % (left column) and 8 wt % (right column). The solvents are pure water (first row), 20/80 vol % formamide/water (second row), 20/80 vol % ethanol/water (third row), and 20/80 vol % glycerol/water mixed solvent (fourth row).

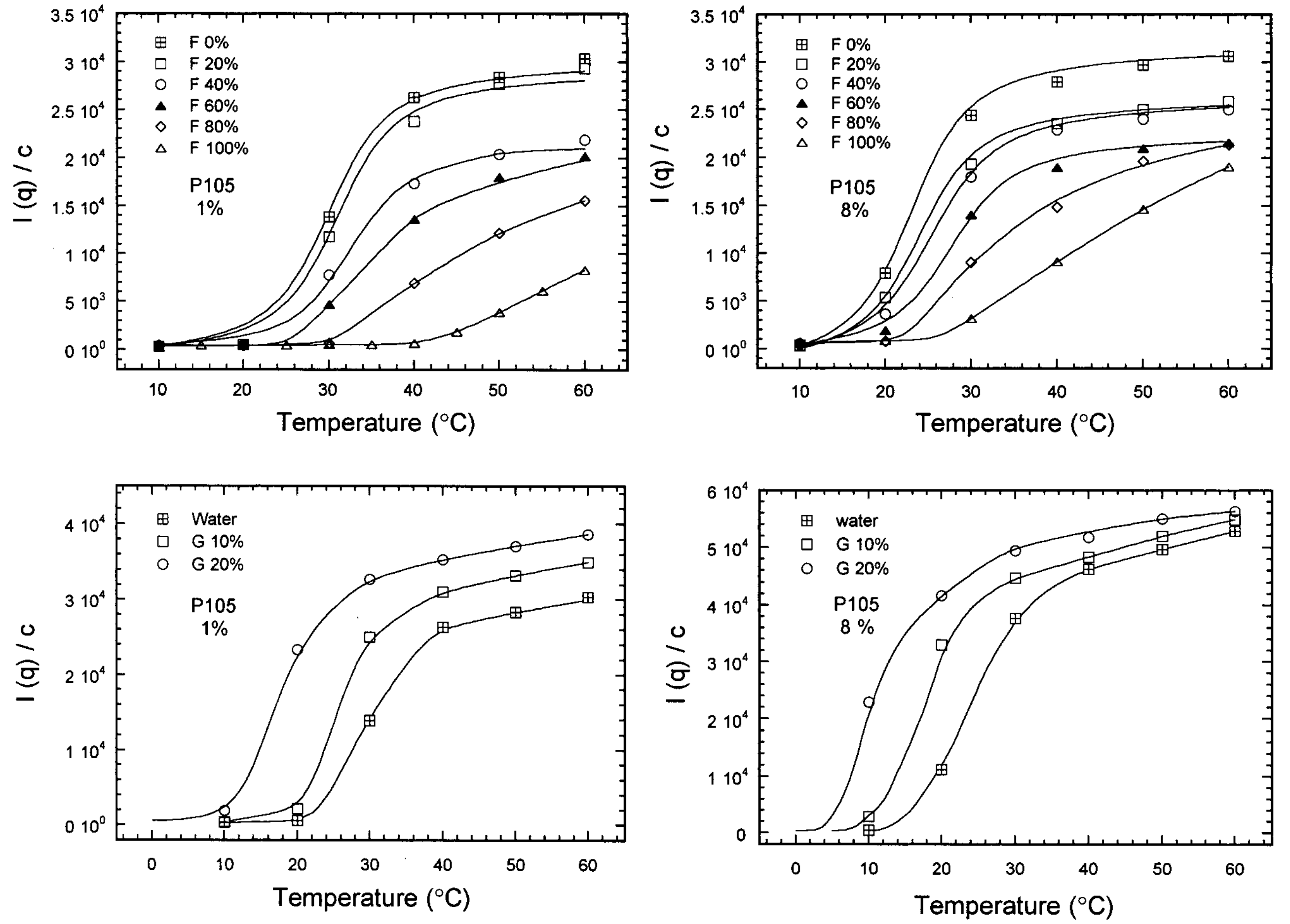

Figure 6. Scattering intensity (*I*/*c*) normalized with respect to the block copolymer concentration (left column: 1 wt %, at $q = 0.021$ Å^{-1}; right column: 8 wt %, at $q = 0.041$ Å^{-1} for formamide–water mixed solvent, at $q = 0.023$ Å^{-1} for glycerol–water mixed solvent), plotted as a function of temperature for $EO_{37}PO_{58}EO_{37}$ dissolved in different mixed solvents. Top row: formamide–water mixed solvent (the formamide content is 0, 20, 40, 60, 80, 100 vol %). Bottom row: glycerol–water mixed solvent (the glycerol content is 0, 10, 20 vol %).

scattering patterns generated from PEO–PPO–PEO solutions of different solvents, such as in the shape of the correlation peak, the maximum scattering peak intensity, and the peak position (q_{peak}). These differences indicate that the addition of cosolvent to the aqueous PEO–PPO–PEO solution has an impact on the micelle or/and unimer structures. From a quantitative analysis of the scattering patterns (see below) we can obtain detailed information on the structure of the unimers and micelles, as well as on the onset of the micellization with an increase of the temperature (cmt) under different solvent conditions.

Micellization of PEO–PPO–PEO Block Copolymers in Various Mixed Solvent Conditions. The formation of micelles is a spontaneous process (negative free energy) driven by the interaction between the solvophobic segments of the amphiphiles and the selective solvent. The onset of the micellization is often reflected in a dramatic change of a number of properties such as surface tension or scattering intensity and can be detected by monitoring such properties.[35,36] In the case of PEO–PPO–PEO block copolymers, temperature is an important variable because it affects the water solvent quality for both blocks: the PPO block is water-soluble at low (4 °C) temperatures but becomes insoluble at room temperature, while PEO remains water-soluble at temperatures as high as 100 °C but eventually phase separates, exhibiting a LCST behavior. At low temperatures, when both PPO and PEO blocks are more soluble in water, the PEO–PPO–PEO block copolymers are present as unassociated unimers. The unimer solution has very low scattering length density contrast due to the relatively even distribution of the deuterated solvent and thus gives rise to low neutron scattering intensity. Upon a temperature increase, the solvophobic PPO blocks tend to associate to minimize contact with the aqueous solvent. The micelles in aqueous solution therefore consist of a desolvated PPO core and a solvated PEO corona. When a deuterated solvent is used, the onset of micelle formation will lead to strong scattering originating from the contrast between solvent-poor core (low SLD) and solvent-rich corona (high SLD), or/and solvent phase (even higher SLD), as well as from interparticle interaction between micelles. Below we analyze the temperature dependence of the relative neutron scattering intensity data, normalized with respect to the block copolymer concentration (shown in Figure 6), to obtain the cmt values for different PEO–PPO–PEO block copolymer concentrations in various mixed solvents.

The normalized scattering intensity (*I*/*c*) at a constant *q* value (0.021 Å^{-1} for 1 wt % $EO_{37}PO_{58}EO_{37}$ solution, 0.041 Å^{-1} for 8 wt % $EO_{37}PO_{58}EO_{37}$ solution in formamide–water mixed solvent, and 0.030 Å^{-1} for 8 wt % $EO_{37}PO_{58}EO_{37}$ solution in glycerol–water mixed solvent) is plotted vs temperature in Figure 6. The data of

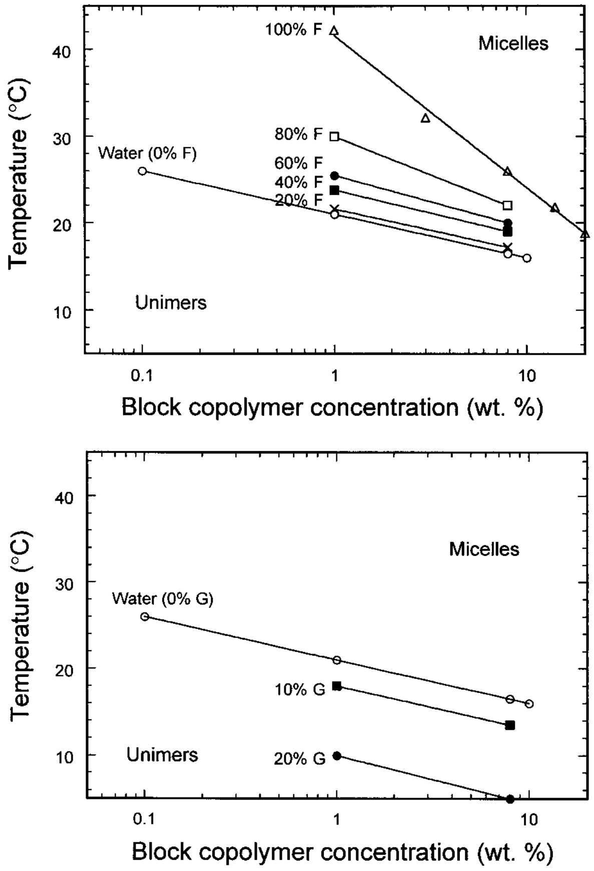

Figure 7. Micellization boundary for $EO_{37}PO_{58}EO_{37}$ dissolved in mixed solvents of varying cosolvent contents. (top) Formamide–water mixed solvent; (bottom) glycerol–water mixed solvent. The micellization boundary represents cmt and cmc data. At temperatures and concentrations below the micellization boundary, the block copolymers do not associate (unimers). At temperatures and concentrations above the micellization boundary, micelles are formed which coexist in equilibrium with unimers.

Figure 6 point out to a characteristic temperature, above which a significant increase of the scattering intensity occurs, indicating micelle formation. We define the critical micellization temperature (cmt) from the intercept of the horizontal line passing though the temperature-independent *I*/*c* data points and of the tangent to the increase *I*/*c*. From Figure 6, we found that formamide and glycerol show opposite effects on the micellization of PEO–PPO–PEO block copolymers. The addition of formamide to water progressively increases the cmt, while the addition of glycerol decreases the cmt. The cmt values of $EO_{37}PO_{58}EO_{37}$ in formamide–water and glycerol–water mixed solvent are plotted in Figure 7 as a function of the block copolymer concentration for different cosolvent contents. The line connecting the cmt–cmc points can be viewed as a micellization boundary within the one-phase solution region. At the low temperature–low concentration region below the micellization boundary the block copolymers exist in the solution as unimers. At the high temperature and high concentration region above the micellization boundary, the block copolymers begin to self-assemble into micelles which coexist in equilibrium with unimers. (The unimer concentration in equilibrium with micelles decreases rapidly with increasing temperature and eventually becomes vanishingly small.[18])

The micellization boundary of Pluronic P105 in formamide/water mixed solvents shifts gradually to higher temperatures and concentrations with increasing formamide content in the mixed solvent. This indicates that the formamide–water mixed solvent becomes a better solvent for the PEO–PPO–PEO block copolymer compared to pure water and thus disfavors the formation of micelles. The same trend was also observed by differential scanning calorimetry (DSC) in Pluronic F87 solutions.[20] The stabilities of the various lyotropic liquid crystalline regions (in particular of the micellar cubic) in $EO_{37}PO_{58}EO_{37}$–formamide binary systems are similarly shifted to higher block copolymer concentrations and temperatures compared with the case of $EO_{37}PO_{58}EO_{37}$ in water.[23]

Opposite to formamide, the addition of glycerol shifts the micellization boundary to lower temperatures and concentrations, indicating that glycerol favors the PEO–PPO–PEO micellization compared to the case of pure water. It was found that the miscibility of glycerol with water decreases in the presence of PEO–PPO–PEO (1 wt % $EO_{37}PO_{58}EO_{37}$ decreases it by a factor of 10%), while that of the formamide remains practically unchanged.[24] At the same time, the solvency conditions for PEO–PPO–PEO become worse in glycerol–water mixed solvent. As shown in the $EO_{37}PO_{58}EO_{37}$–glycerol–water ternary isothermal phase diagram,[24] the hexagonal (cylindrical) lyotropic liquid crystals become stable at lower block copolymer contents with increasing glycol content. The PEO–PPO–PEO molecules tend to self-assemble at lower temperatures and lower concentrations in an attempt to reduce the solvophobic interaction between the copolymer and the solvent.

The addition of ethanol to water is reported to increase the temperature, $T_{1/2}$, at which the micellization process is half completed in aqueous solutions of Pluronic F87.[20] Ethanol also shows disordering effects by reducing the extent of the lyotropic liquid crystalline regions in the $EO_{37}PO_{58}EO_{37}$–ethanol–water ternary isothermal phase diagram.[24] However, the SANS data we have collected are insufficient to draw conclusions about the ethanol effects on the micellization boundary. In particular, we observed a correlation peak at low temperature in the scattering pattern (not shown here) of 8 wt % $EO_{37}PO_{58}EO_{37}$ in 40/60 vol % ethanol/water mixed solvent, which seems to contradict the results from the DSC measurements[20] and the phase diagram study.[24] Further experiments are required to probe whether the correlation peak at low temperatures in $EO_{37}PO_{58}EO_{37}$ aqueous solution with high ethanol content originates from micelles or from other possible structures.

Effect of Cosolvents on the PEO–PPO–PEO Unimer Radius. Using the unimer form factor expected from a Gaussian chain and given by eq 1, and assuming that the structure factor is 1, the radius of gyration (R_g) was obtained for the experimental data of 1 wt % $EO_{37}PO_{58}EO_{37}$ in various solvent conditions at 10 °C. The results are presented in Figure 1. The unimer R_g appears independent of the variation of the cosolvent type and content under the low temperature and concentration conditions examined.

Effect of Cosolvents on the PEO–PPO–PEO Micelle Structure. The micelle core and core + corona radii (R_{core} and $R_{micelle}$) and the micelle association number ($N_{association}$) values obtained by fitting eqs 2–9 to the scattering patterns of 1 and 8 wt % $EO_{37}PO_{58}EO_{37}$ at 60 °C, with various cosolvent contents (formamide: 0–100 vol %; ethanol: 0–40 vol %; glycerol:

Table 1. Physicochemical Parameters of the Solvents Used in This Study[a]

solvent	M_w[b]	mp	bp	density[b] (g/cm^3)	dielectric constant[c]	dipole moment[c]	octanol/water partition coeff log *P*
water	20.02	0	100	1.11	78.5	3.11	
formamide	48.04	2.5	220	1.2032	109	3.73	−1.50
glycerol	100.4	18	290	1.371	42.5	2.68	−2.55
ethanol	52.12	−114	78	0.891	24.3	1.69	−0.32

[a] M_w = molecular weight, mp = melting point, and bp = boiling point. [b] The M_w and the density (at 25 °C) are for deuterated solvents. [c] The dielectric constant (at 25 °C) and dipole moment (in debye units) data for the solvents are taken from *Handbook of Chemistry and Physics, 72nd ed.*; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1991.

Table 2. Fitting Parameters Obtained from Using Eqs 4−13 for 1% and 8% $EO_{37}PO_{58}EO_{37}$ Solution in Mixed Solvents at 60 °C

(a) In Formamide−Water Mixed Solvent

$EO_{37}PO_{58}EO_{37}$ concn (wt %)	formamide content in mixed solvent (vol %)	R_{core} (Å) ± 0.5	$R_{micelle}$ (Å) ± 1	R_{HS} (Å)	$N_{association}$ ± 1	α_{core} ± 0.02	α_{corona} ± 0.02
1	0	47	82	140 ± 5	76	0.97	0.22
1	20	46	79	130 ± 5	70	0.95	0.23
1	40	44.5	76.5	130 ± 5	63	0.94	0.23
1	60	43.5	75	135 ± 5	57	0.92	0.22
1	80	42	73	105 ± 5	51	0.91	0.21
1	100	39.5	68	100 ± 5	41	0.88	0.21
8	0	46.5	80	85 ± 2	78	1.00	0.25
8	20	45.5	77	85 ± 2	71	0.99	0.25
8	40	44	74	86 ± 2	63	0.96	0.26
8	60	43	72	83 ± 2	58	0.96	0.26
8	80	41	70	79 ± 2	48.5	0.93	0.23
8	100	39	68	65 ± 2	40	0.89	0.20

(b) In Ethanol−Water Mixed Solvent

$EO_{37}PO_{58}EO_{37}$ concn (wt %)	ethanol content in mixed solvent (vol %)	R_{core} (Å) ± 0.5	$R_{micelle}$ (Å) ± 1	R_{HS} (Å)	$N_{association}$ ± 1	α_{core} ± 0.02	α_{corona} ± 0.02
1	0	47	82	140 ± 5	76	0.97	0.22
1	5	47	81	145± 5	76	0.97	0.23
1	10	46	79	90 ± 5	69	0.94	0.22
1	20	43.5	76	92 ± 5	58	0.93	0.21
1	40	32.5	59	50 ± 5	22	0.85	0.17
8	0	46.5	80	85 ± 2	78	1.00	0.25
8	5	46	81	84 ± 2	75	1.00	0.22
8	10	45.5	78.8	85 ± 2	70	0.98	0.23
8	20	44	78	83 ± 2	62	0.96	0.21
8	40	34	60	72 ± 2	25.5	0.86	0.19

(c) In Glycerol−Water Mixed Solvent

$EO_{37}PO_{58}EO_{37}$ concn (wt %)	glycerol content in mixed solvent (vol %)	R_{core} (Å) ± 0.5	$R_{micelle}$ (Å) ± 1	R_{HS} (Å)	$N_{association}$ ± 1	α_{core} ± 0.02	α_{corona} ± 0.02
1	0	47	82	140 ± 5	76	0.97	0.22
1	10	48	77	160 ± 5	82	0.98	0.31
1	20	50	75	180 ± 5	92	0.98	0.40
1	40	50	76	185 ± 5	99	1.00	0.41
8	0	46.5	80	85 ± 2	78	1.00	0.25
8	10	47.5	75	86 ± 2	83	1.00	0.34
8	20	48.5	70	86 ± 2	92	1.00	0.52

0−20 vol %), are presented in Table 2 and Figure 8. The polymer volume fraction values in the micelle core and corona (α_{core} and α_{corona}), calculated according to eq 6, are also shown in Table 2 and Figure 8. The error bars shown for each parameter in Tables 2 and 3 signify the ± range variation of that parameter that would result in no discernible worsening of the model fit to the experimental data. At 60 °C, 1 and 8 wt % $EO_{37}PO_{58}EO_{37}$ solutions are far away from the unimer/micelle transition boundary for all the mixed solvents. Below we discuss the cosolvent effects at this temperature, where the block copolymer micelles are well-defined and dominate the scattering function.

Addition of formamide or ethanol to aqueous $EO_{37}PO_{58}EO_{37}$ solution has very similar effects on the micelle structure, as seen in Table 2 and Figure 8. The micelle core and core + corona radii decrease with increasing cosolvent content for both formamide and ethanol. The micelle association numbers become smaller in the presence of formamide or ethanol. Ethanol has a pronounced impact on the micelle structure. In the 20/80 vol % ethanol/water mixed solvent, $N_{association}$ is 62, 20% lower than the 78 value observed in pure water. Upon a further increase of the ethanol content in the mixed solvent to 40 vol %, $N_{association}$ sharply decreases to 25, almost $^1/_3$ of that in pure water. This decrease in $N_{association}$ is accompanied by a ~25% decrease of the micelle core and core + corona radii. In the 0−40 vol % range, formamide causes less than 20% reduction in $N_{association}$ compared with the case of pure water and less than 8% decrease in R_{core} and $R_{micelle}$. In pure formamide, the association number of $EO_{37}PO_{58}EO_{37}$ is about half of that in pure water, and the size of micelle core and corona is around 85% of that in pure water.

The polymer volume fraction values in the core and corona can shed some light on the effects of formamide

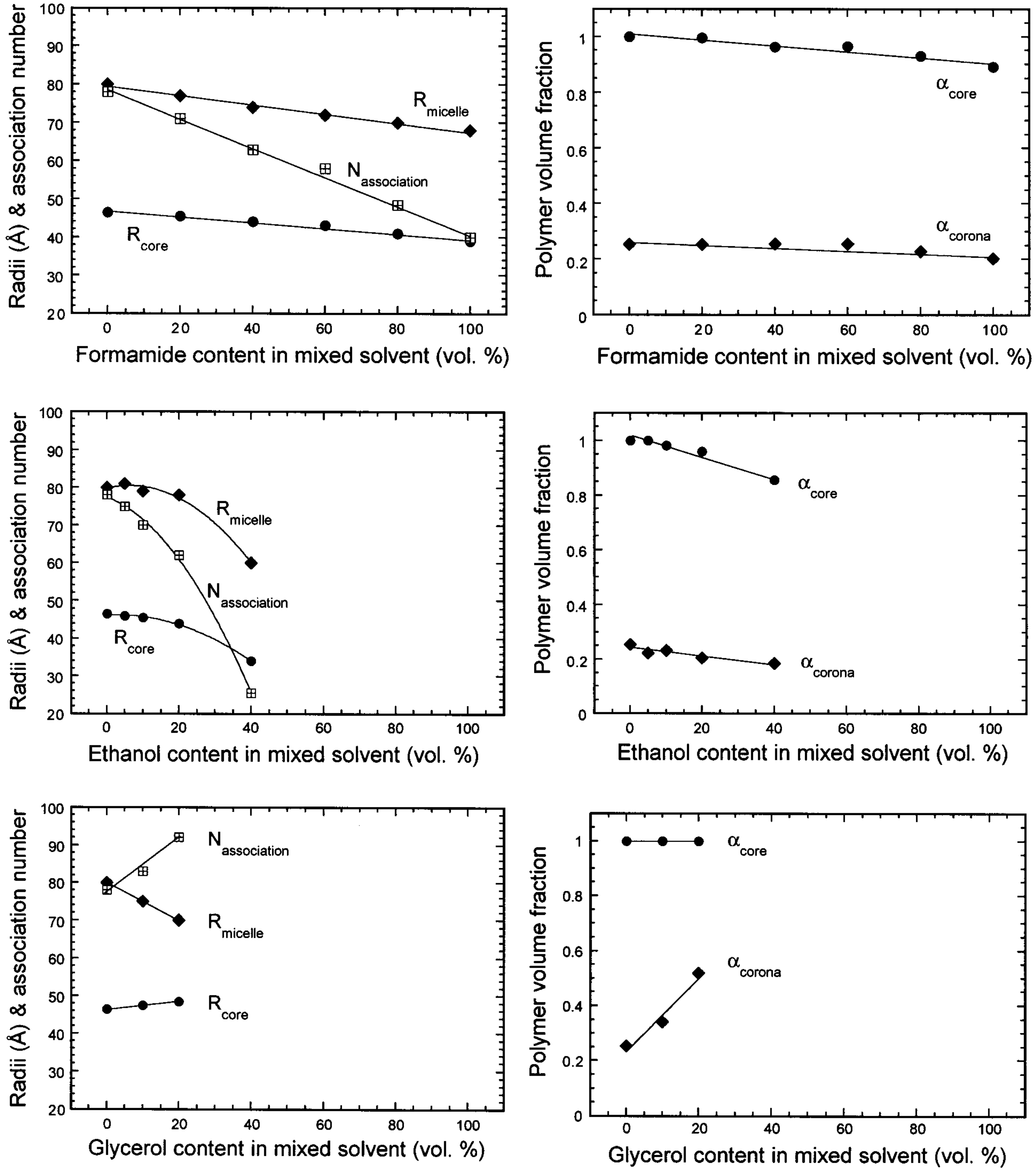

Figure 8. Structural information obtained from SANS in 8 wt % $EO_{37}PO_{58}EO_{37}$ solution at 60 °C, plotted as a function of the cosolvent content in the mixed solvent. First row: formamide–water mixed solvent; second row: ethanol–water mixed solvent; third row: glycerol–water mixed solvent. Left column: radii of core and core + corona (R_{core} and R_{micelle}) and micelle association number ($N_{\mathrm{association}}$); right column: polymer volume fraction of core and corona (α_{core} and α_{corona}). The error bar is smaller than the size of the symbols in all the plots.

and ethanol on the micelle structure. With 20 vol % ethanol 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 0.96, and the polymer volume fraction in the corona (α_{corona}) decreases from 0.25 in pure water to 0.21. When the ethanol content in the mixed solvent increases to 40 vol %, α_{core} decreases to 0.86 (leaving a relatively high 14 vol % solvent content in the core), while α_{corona} becomes 0.19. Addition of formamide also results in “swelling” (higher degree of solvation) of both the core and corona, but the effect of formamide is smaller than that of ethanol. In the range 0–40 vol % formamide in the mixed solvent, the polymer content in the corona remains constant within the error bar, while the polymer volume fraction in the core (α_{core}) decreases from 1 in pure water to 0.96 in mixed solvent with 40 vol % formamide. The decreasing polymer volume fractions in the micelle core and corona with increasing cosolvent content indicate that both PPO and PEO blocks are solvated to a higher degree in formamide–water or ethanol–water mixed solvents.

The lower micelle association values observed in formamide–water and ethanol–water mixed solvents

Table 3. Change of Micelle Structure with Temperature

temp (°C)	R_{core} (Å) ± 0.5	R_{micelle} (Å) ± 1	R_{HS} (Å) ± 2	N_{assoc} ± 1	α_{core} ± 0.02	α_{corona} ± 0.02
in 8 wt % $EO_{37}PO_{58}EO_{37}$ in pure water						
30	40	71	84	50	1.00	0.22
40	41.5	74	86	57	1.00	0.22
50	44	77	84	67	1.00	0.23
60	46.5	80	85	78	1.00	0.25
in 8 wt % $EO_{37}PO_{58}EO_{37}$ in formamide/water mixed solvent with 40 vol % formamide						
30	40	69	81	46	0.91	0.22
40	42.5	73	84	56	0.96	0.23
50	43	73	84	58	0.96	0.24
60	44	74	86	63	0.96	0.26
in 8 wt % $EO_{37}PO_{58}EO_{37}$ in pure formamide						
35	33	58	60	25	0.90	0.20
40	34	58.5	60	27	0.91	0.22
45	36	63	62	32	0.91	0.20
50	37	64.5	65	34.5	0.90	0.21
55	37.5	65	64.5	36	0.90	0.21
60	39	68	65	40	0.89	0.20
in 8 wt % $EO_{37}PO_{58}EO_{37}$ in ethanol/water mixed solvent with 20 vol % ethanol						
30	39	70	79	39	0.87	0.18
40	41.5	75	80.5	50	0.92	0.18
50	43	78	81	57	0.95	0.19
60	44	78	83	62	0.96	0.21
in 8 wt % $EO_{37}PO_{58}EO_{37}$ in glycerol/water mixed solvent with 10 vol % glycerol						
20	42.5	69	84	57	0.98	0.29
30	45	76	85	69	1.00	0.26
40	46	76	84	73	1.00	0.27
50	46	75.5	86	77	1.00	0.23
60	47.5	75	86	83	1.00	0.34

are in agreement with the fact that adding ethanol or formamide into water makes it a better solvent for PEO−PPO−PEO block copolymers. Small micelles, with a large part of the surfactant hydrophobic chain in contact with the solvent, are unfavorable in water because the interfacial tension between water and the hydrophobic chain is high. It is notable that in 40/60 vol % ethanol/water mixed solvent, the very small ($^1/_3$ of that in water) association number accompanies a rather "solvated" PPO core (14 vol % solvent content). The addition of formamide and ethanol to water reduces the interfacial tension between the hydrophobic chains and the solvent, and the formation of smaller micelles becomes more energetically favorable.

The disordering effect of ethanol observed above for the case of PEO−PPO−PEO micelles is also evident in the $EO_{37}PO_{58}EO_{37}$−ethanol−water ternary isothermal (25 °C) phase diagram,[24] where 20 wt % ethanol in the ternary mixture can "dissolve" the lyotropic liquid crystalline structures (which form in water at $EO_{37}PO_{58}EO_{37}$ concentrations > 30 wt %). The effects of ethanol on the phase behavior and microstructure have been explained in terms of the polarity and the affinity of the cosolvent to the different segments of the block copolymer.[24] The octanol/water partition coefficients (log *P*) of ethylene glycol, which has the closest structure to the PEO segments, is −1.93; that of the propylene glycol, which has the closest structure to PPO segments, is −1.41.[24] Note that a negative log *P* value indicates that a certain compound, given a choice between water and octanol, prefers to partition in water. The log *P* value of ethanol is −0.32 and that of formamide is −1.50 (see Table 1); thus, they are both more hydrophobic compared with the PEO block. Addition of ethanol or formamide into water will render it a better solvent for the hydrophobic PPO blocks. As a result, the solvent contents in both the core and the corona of the micelles increase with increasing amount of ethanol or formamide in the mixed solvent. Moreover, while both ethanol and formamide are polar and miscible with water, ethanol is relatively more hydrophobic (has a less negative log *P* value) and should have a higher preference to mix with hydrophobic PPO blocks.

Glycerol affects the micelle structure to an opposite direction compared with the cases of formamide and ethanol. As indicated in Table 2 and Figure 8, when the glycerol content increases from 0 to 20 vol %, the micelle association number increases from 78 to 92. Although the core radius increases (from 46.5 Å in water to 48.5 Å in 20/80 vol % glycerol/water mixed solvent) correspondingly with the association number increase, the micelle radius decreases (from 80 Å in water to 70 Å in 20/80 vol % glycerol/water mixed solvent, a 12% decrease). This is a result of how glycerol affects the solvent distribution 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 doubles from 0.25 in pure water to 0.52 in 20 vol % glycerol. This pronounced increase of the polymer volume fraction in the corona suggests that some of the solvent initially swelling the corona is withdrawn upon the addition of glycerol into water. Note that the octanol/water partition coefficient (log *P*) of glycerol is −2.55 (see Table 1), which is more negative than that of ethylene glycol (the compound resembling PEO) and indicates a strong affinity to water. The decrease of the micelle radius is thus associated with the dehydration of the PEO blocks, although the micelle association number increases.

The cosolvent effects on the polyether block copolymer micelle structural parameters discussed above in the context of the cosolvent/water ratio for a given cosolvent are summarized in the graphs of Figure 9, where data for all the three cosolvents examined here (formamide, ethanol, and glycerol) are shown in the same plot for each of the five structural parameters considered here: micelle association number, core radius, micelle radius, and polymer volume fraction of core and corona (α_{core} and α_{corona}). Figure 9 emphasizes the opposite trends in terms of solvent quality exhibited by ethanol and formamide on one hand and glycerol on the other and allows for direct comparison between different cosolvents at the same cosolvent/water ratio.

Addition of glycerol to water has been reported to result in a higher micelle association number and a decrease in the PEO headgroup hydration also in low-molecular-weight ethoxylated nonionic surfactants such as $C_{12}EO_8$.[6] The association number of the $C_{12}EO_8$ micelles increases by a factor of 9% with 20 wt % D-glycerol added into deuterated water, and the radius of the micelle core remains almost constant, whereas the micelle radius decreases by a factor of 10%.[6] These trends are very similar to what we observed above for $EO_{37}PO_{58}EO_{37}$. Interestingly, in aqueous $C_{12}EO_8$ solutions with 20 wt % glycerol, the hydration per EO segment is decreased by 78% compared to that in plain water, at a time that 20 vol % glycerol in an 8 wt % $EO_{37}PO_{58}EO_{37}$ solution results in a 66% decrease of the hydration per EO segment. Therefore, the addition of glycerol to aqueous solution leads to a pronounced dehydration of the EO group, both for low molecular weight ethoxylated surfactants and for high molecular weight polyether block copolymers.

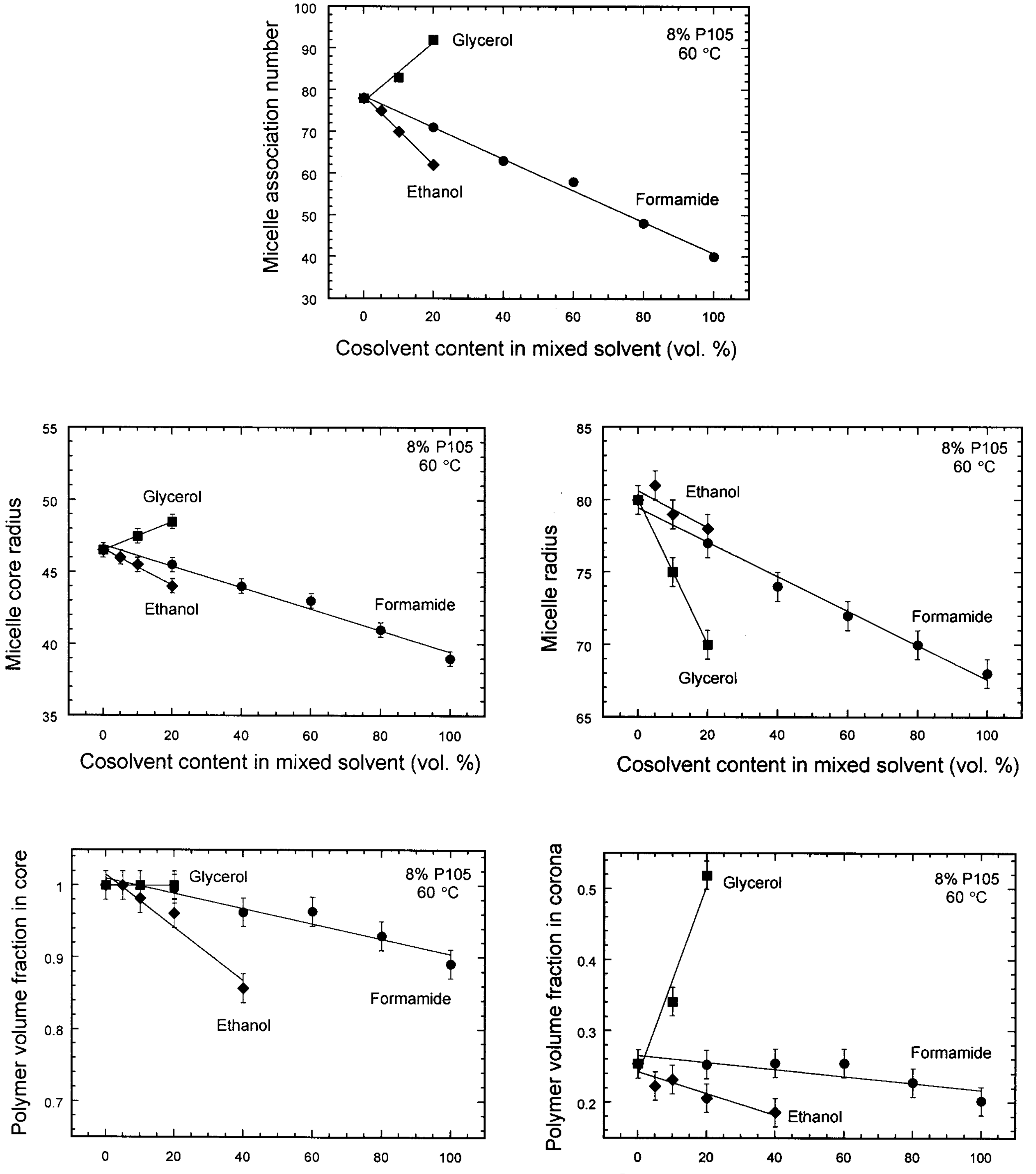

Figure 9. Structural information obtained from SANS in 8 wt % $EO_{37}PO_{58}EO_{37}$ solution at 60 °C, plotted as a function of the cosolvent (glycerol, formamide, or ethanol) content in the mixed solvent. First row: micelle association number ($N_{association}$); second row: radii of core and core + corona (R_{core} and $R_{micelle}$); third row: polymer volume fraction of core and corona (α_{core} and α_{corona}).

It has also been reported that the lattice spacing of lyotropic liquid crystals formed in water by $C_{12}EO_8$[7] and by $EO_{37}PO_{58}EO_{37}$[25] increased upon the introduction of glycerol. This increase of the lattice spacing and corresponding decrease of the average area per amphiphilic molecule at the polar/apolar interface were attributed to the deswelling of the PEO blocks by glycerol.[25] The SANS data reported in this study indicate that, when glycerol is added to water, the PEO-rich corona gradually dehydrates, and more PEO–PPO–PEO block copolymer molecules associate into one micelle. The higher association number observed at the presence of glycerol may result from the attempt to reduce the unfavorable interactions between the PPO blocks and the glycerol/water mixed solvent, as well as between the PEO blocks and the mixed solvent. In this study, we found that the micelle association number in 8 wt % $EO_{37}PO_{58}EO_{37}$ solution increased by 18% (from 78 in pure water to 92 in glycerol/water mixed solvent) when 20 vol % glycerol was added. In the cubic lyotropic liquid crystalline microstructure formed by $EO_{37}PO_{58}EO_{37}$ micelles, such a 18% increase of the micelle association number would lead to an approximately 6% increase of the lattice parameter (*d*). In a recent study on the effect of glycerol on $EO_{37}PO_{58}EO_{37}$ lyotropic liquid crystal microstructure,[25] small-angle X-ray scattering (SAXS) data indicated that the lattice parameter in the micellar cubic phase (30 wt % $EO_{37}PO_{58}EO_{37}$) indeed increased by a factor of 6% upon the addition of 20 vol % glycerol. This excellent agreement as well as the other trends discussed above (and summarized in Figure 8) indicates that the effects of glycerol on the micelle structure in dilute solution are quantitatively comparable to these on the lyotropic liquid crystal microstructures which form at higher (>30 wt %) block copolymer contents.

Effect of Block Copolymer Concentration on PEO–PPO–PEO Micelle Structure in Various Mixed Solvents. The block copolymer concentration in the solution plays an important role in the formation of both micelles and lyotropic liquid crystals.[24] For example, the cmt decreases with an increase of the block copolymer concentration (Figure 7). In the mixed solvent systems examined here, the micelle core and core + corona radii (R_{core} and $R_{micelle}$) and the micelle association number ($N_{association}$) did not change much when the $EO_{37}PO_{58}EO_{37}$ concentration increased from 1 to 8 wt % (see data presented in Table 2 and Figure 8). However, a closer look reveals that the polymer volume fraction in both the micelle core and corona is smaller in the lower (1 wt %) block copolymer concentration for all the mixed solvents examined here. These data indicate that the micelle structure is looser at low copolymer concentrations compared with that at high copolymer concentrations. From Table 2, we also find that the hard-sphere interaction distance (R_{HS}) is much larger in the dilute (1 wt % $EO_{37}PO_{58}EO_{37}$) solution compared with the more concentrated (8 wt %) solution. As shown in SANS scattering patterns generated from 1 and 8 wt % $EO_{37}PO_{58}EO_{37}$ solution (Figure 5), the correlation peak at 1 wt % $EO_{37}PO_{58}EO_{37}$ is very weak, while the peak at 8 wt % is strong. Both the SANS scattering patterns and the data obtained from fitting indicate that in dilute solutions the micelles remain further apart, and the intermicellar interactions are much weaker.

Effect of Temperature on PEO–PPO–PEO Micelle Structure in Various Mixed Solvents. Because of the decreasing solubility of PPO, and to a lesser extent of PEO, in water with increasing temperature,[37] the micellization of PEO–PPO–PEO block copolymers is strongly temperature-dependent. For 8 wt % $EO_{37}PO_{58}EO_{37}$ in pure water, with a temperature change from 30 to 60 °C, the micelle core remains "dry", while the polymer volume fraction (α_{corona}) in the corona increases slightly (see Table 3). The micelle association number increases from 50 to 78 in the temperature range 30–60 °C, indicating that PEO–PPO–PEO micelles tend to consist of more molecules at higher temperatures. The temperature dependence of the micelle structure is similar in the formamide–water, ethanol–water, and glycerol–water mixed solvents, as shown in Table 3 and Figure 10. A larger number of macromolecules associate into one micelle, and the micelle core and core + corona radii increase with increasing temperature. Moreover, the micelle core and corona become less solvated at higher temperature, as evidenced by the higher polymer volume fractions α_{core} and α_{corona}.

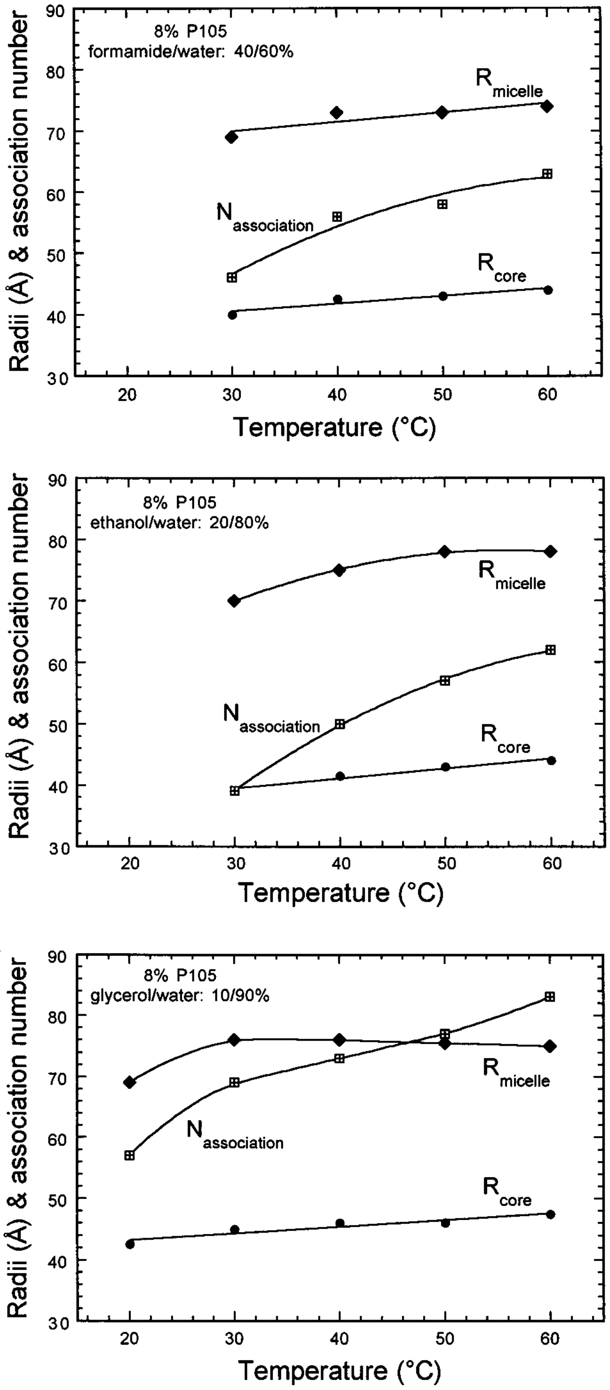

Figure 10. Structural information (micelle core and core + corona radii (R_{core} and $R_{micelle}$) and micelle association numbers ($N_{association}$) obtained from SANS in 8 wt % $EO_{37}PO_{58}EO_{37}$ solution at mixed solvents plotted as a function of temperature: (top) 40/60 vol % formamide/water mixed solvent; (middle) 20/80 vol % ethanol/water mixed solvent; (bottom) 10/90 vol % glycerol/water mixed solvent.

From a comparison of the cosolvent effects with the temperature effects on the polyether block copolymer structure, we can see that the addition to the aqueous solvent of formamide 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 formamide or ethanol; correspondingly, the radii of the micelle core and core + corona, as well as the micelle association numbers, decrease. 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 and the micelle association number increases, trends which are also observed in plain water solvent with an increase of the temperature. The interrelation between cosolvent effects and temperature effects documented in the present work should be very useful in applications of polyether block copolymers where the "right" balance of amphiphile properties is required in order to achieve the objectives for a given formulation or product. For example, the addition of 80 vol % formamide into water at 60 °C is equivalent (in terms of solution structure) to a decrease in the solution temperature from 60 to 30 °C in pure water solvent; the addition of 20 vol % ethanol at 60 °C is almost comparable to a decrease in the temperature in pure water solvent from 60 to 40 °C.

Conclusions

The effects of cosolvents such as formamide, ethanol, and glycerol on the aqueous solution structure of a polyether block copolymer (Pluronic P105: $EO_{37}PO_{58}$-EO_{37}) have been investigated as a function of the cosolvent content in the mixed solvent, the block copolymer concentration, and the solution temperature using SANS. Such fundamental information on cosolvent effects on 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.

The onset of block copolymer micellization in the mixed solvents was indicated by an the increase of the SANS scattering intensity with increasing temperature. Micelles form at higher concentrations and temperatures when formamide and ethanol were added to water, indicating that formamide−water and ethanol−water mixed solvents offer better solvent conditions for the PEO−PPO−PEO block copolymer. On the contrary, the addition of glycerol promotes the formation of micelles and shifts the micellization boundary to lower concentrations and temperatures. This behavior can be attributed to the competition between glycerol and PEO blocks for water solvation.

A core−corona form factor and a hard-sphere interaction structure factor were used to extract information about the micelle size (R_{core} and R_{micelle}), intermicellar distance (R_{HS}), and micelle association number ($N_{\text{association}}$). 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 addition of formamide or ethanol into water has similar effects on the micelle structure, but the effect of ethanol is more pronounced. The micelle core and core + corona radii and the micelle association number decrease progressively upon the addition of formamide or ethanol, accompanying a decrease of the polymer volume fraction in the micelle core and corona. The addition of glycerol, however, increases the micelle association number and reduces the corona thickness. At the same time, the polymer volume fraction in the corona doubles when the glycerol content increases from 0 to 20 vol %.

Judging from their octanol/water partition coefficients (log P), formamide and ethanol, although both miscible with water, are hydrophobic compared with the PEO blocks, and they have a higher affinity than water for the hydrophobic PPO blocks. Thus, the addition of formamide or ethanol in water results in better solvent conditions for the block copolymer and leads to an increase of the solvent content in both the micelle core and the corona. Glycerol has the most negative log P among the cosolvents examined here. In the presence of glycerol, the amount of water hydrating the PEO corona decreases. The changes in the micelle structure upon the addition of formamide, ethanol, or glycerol reported here are in excellent agreement with recently reported results on the effects of cosolvents on the lyotropic liquid crystals formed by PEO−PPO−PEO block copolymers.

An increase of temperature results in larger micelle association numbers and micelle radii and lower degree of solvation in the micelle core and corona in the cosolvent−water mixed solvents. Thus, the cosolvent−water mixed solvents become progressively worse for the PEO−PPO−PEO block copolymer with increasing temperature. It is interesting to note that the effects of varying (decreasing or increasing) temperature on the micelle structure can be achieved at a constant temperature by the addition of different types of cosolvents (formamide/ethanol or glycerol, respectively). The interrelation between cosolvent effects and temperature effects documented in the present work should be useful in applications of polyether block copolymers where the "right" balance of amphiphile properties is required in order to achieve a given formulation.

Acknowledgment. P.A. acknowledges the National Science Foundation (Grant CTS-9875848) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant ACS−PRF# 33408-G7), for support of this research. We also acknowledge the support of the National Institute of Standards and Technology (NIST), U.S. Department of Commerce, in providing the neutron research facilities used in this work;[38] this material is based upon activities supported by the National Science Foundation under Agreement DMR-9423101. We thank Dr. Paul D. Butler at NIST for valuable assistance with the SANS data acquisition.

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