

Thermodynamic and Structural Studies of Triton X-100 Micelles in Ethylene Glycol–Water Mixed Solvents

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Micellar properties of *p*-tert-octyl-phenoxy (9.5) polyethylene ether (Triton X-100) in aqueous mixtures of ethylene glycol (EG) were determined using such techniques as surface tension, static and dynamic light scattering, and fluorescence spectroscopy. Thermodynamics of micellization was obtained from the temperature dependence of critical micelle concentration values. The differences in the Gibbs energies of micellization of Triton X-100 between water and binary solvent systems were calculated to evaluate the influence of cosolvent on the micellization process. From this study, it can be concluded that the structure-breaking ability of EG and its interaction with the oxyethylene groups of the surfactant are dominating factors in the micellization process. Thermodynamics of adsorption of the solution–air interface was also evaluated. It was found that the surface activity of the surfactant decreases slightly with increasing concentration of EG at a given temperature. By a combination of static and dynamic light scattering measurements, a reduction of the micelle size was observed, mainly due to a decrease of the micellar aggregation number, whereas the micellar solvation was not substantially modified in magnitude with EG addition. However, the change of the surface area per headgroup of the surfactant suggested an alteration in the nature of its solvation layer, produced probably by a certain participation of cosolvent in the micellar solvation layer. This point was corroborated from the fluorescence polarization studies of several luminescent probes, including coumarin 6, merocyanine 540, and rhodamine B. These experiments revealed a slight increase of the micellar microviscosity. Finally, the proposed mechanism was also supported by the increase observed in the cloud point of Triton X-100, induced by the EG addition.

Introduction

It has been proposed that the ability of a solvent to form hydrogen bonds is a necessary condition for the formation of micelles. However, the ability of water to form unique hydrogen-bonded networks is not a necessary condition for the aggregation process.¹ Recently, there has been a considerable amount of research dealing with the effects of nonaqueous polar solvents, such as glycerol, formamide, and ethylene glycol, on the micellization process.^{2,3} Ethylene glycol (EG) is of particular interest in that it has many characteristics similar to those of water. The molecule is small and can form hydrogen-bonded networks similar in nature to those of water but considerably different in the details of the structure. Ethylene glycol also possesses a high cohesive energy and a fairly high dielectric constant. Because of the similarities between water and EG, the study of the latter is important from the point that it provides a better understanding of the structure of liquids on the micellization process.⁴

To elucidate the effects of EG on the micellization process, it is useful to study the behavior of the molecule as a cosolvent on model compounds. Most of the investigations using EG as a cosolvent or as a pure solvent were carried out with ionic surfactants.^{4–17} These inves-

tigations focused mainly on the critical micelle concentration (cmc) determination, counterion dissociation, size of aggregates, or solvent interaction with the surfactant headgroup. Micellization of nonionic surfactants in nonaqueous polar solvents, and in particular EG, has been less frequently investigated.^{18–22} Penfold et al.²² reported a study, using small-angle neutron scattering (SANS), of nonionic surfactants in water mixtures with EG, sorbitol,

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and glycerol. They found that the size of the micelles increased with the addition of cosolvent. They attributed this change to a decreasing hydration of the polar headgroups due to the interaction between water and cosolvent, resulting in a reduction of the curvature of the aggregate.²² However, Cantú et al.²⁰ found that both the hydrodynamic radius and the aggregation number of monododecyl octaethylene glycol micelles decreased with the addition of glycerol to the solvent system. This effect was ascribed to a reduction of the micelle solvation in the mixed solvent.

In this paper, we report a multifaceted study on the micellar properties of the nonionic surfactant, *p*-tert-octylphenoxy polyethylene (9.5) ether (Triton X-100 or TX-100) in EG–water mixtures. This surfactant was selected because of its extensive use in industrial and pharmaceutical formulations and in biochemical research. There is a report of a study of the micelle formation of TX-100, among other nonionic surfactants, in water–EG mixtures,¹⁹ that used a difference spectrophotometric technique to investigate only the change of the cmc with temperature. In the present investigation, we examined the effect of the EG addition on the aggregation behavior of TX-100 from several points of view: namely, the thermodynamics of micellization and adsorption from surface tension measurements, aggregation numbers and micelle size using light scattering techniques, the change in the microstructure of the micelles using steady-state fluorescence polarization, and the effect of the addition of EG on the cloud point of TX-100.

Experimental Section

Materials. The surfactant Triton X-100, whose chemical structure is $C_8H_{17}C_6H_4(OC_2H_4)_n$ with n equal to 9–10 and an average molecular weight of 625 g/mol, was purchased from Sigma (SigmaUltra, >99.6%). The fluorescence probes pyrene, rhodamine B, and merocyanine 540 were also obtained from Sigma. Ethylene glycol (99%+) and coumarin 6 were purchased from Aldrich. These materials were used as supplied. Stock solutions of pyrene, coumarin 6 (C6), and rhodamine B (RhB) were prepared in absolute ethanol. Merocyanine 540 (MC540) was dissolved in a 2:1 chloroform–methanol mixture. All other chemicals used were analytical grade. All aqueous solutions were prepared using Millipore water, equivalent to doubly distilled. All experiments were carried out with freshly prepared solutions.

Methods. Surface Tension Measurements. Surface tension measurements were carried out according to the du Nouy method on a Fisher Surface Tensiometer, model 21, equipped with a 13 mm diameter platinum–iridium ring. The solutions were placed in a thermostated beaker at a constant temperature. To establish equilibrium, measurements were repeated at 3-min intervals up to 30 min. The measured values were corrected as described for the instrument. The surface tension value of pure water was periodically checked to ensure consistency of measurement.

Light Scattering Measurements. Static and dynamic light scattering experiments were performed on a Malvern 4700 photon correlation spectroscopy (PCS) system using a 75 mW argon laser emitting vertically polarized light at a wavelength of 488 nm. With this system, the angular dependence of the scattering could be measured over the range 30–150°. All measurements were carried out at 25.0 ± 0.1 °C using a circulating water bath. Cylindrical quartz cells of 10 mm diameter were used in all the light scattering experiments. Before use, the cells were soaked in nitric acid and rinsed with Millipore water and finally with freshly distilled acetone. The surfactant solutions were filtered once through a 0.1 μ m Millipore filter directly into the cell and sealed until used. This filtration effectively removed any dust particles present as none of the solutions exhibited significant dissymmetry (the ratio of light scattered at the angles of 45° and 135° never exceeded 1.10 in any of the solutions).

The autocorrelation function was obtained using a 256-channel photon correlator. The collective (or apparent) diffusion coef-

ficient, D_c , was determined from the measured correlation function using the second-order cumulant analysis.²³ The diffusion coefficient was measured at least three times for each sample. The average error in these experiments was approximately 4%.

All measurements (the average scattered intensity and the intensity correlation function) were made at a scattering angle (θ) equal to 90°, after initial studies indicated that the micelles were too small to exhibit significant angular dependence of the scattered light within the experimental error. The intensity of scattered light was measured at least four times for each sample. The average error in these repeated measurements was approximately 2%.

The refractive index values of TX-100 micellar solutions and of solvent mixtures were measured at 25.0 ± 0.1 °C using a Bausch and Lomb Abbe-3L refractometer. The refractive index increments (dn/dc) obtained for TX-100 in water and in solvent mixtures were 0.158, 0.138, 0.139, and 0.132 mL/g for 0%, 20%, 40%, and 60% EG, respectively. The partial specific volume of micellar TX-100 was calculated from²⁴

$$\nu = \frac{1}{\rho_0} \left(1 - \frac{d\rho_{01}}{dc} \right) \quad (1)$$

where ρ_{01} and ρ_0 are the densities of the sample solution and the medium, respectively. The density values were measured with an Anton Paar DMA 5000 densimeter. The values obtained were 0.9135, 0.9183, 0.9108, and 0.8852 mL/g for TX-100 in solvent mixtures containing 0%, 20%, 40%, and 60% EG, respectively.

The solvent viscosity values at 25.0 °C used in this study were measured with a Haake Rotovisco VT550 concentric-cylinder rotational viscometer. The viscosity measurements were obtained with an NV sensor system and an outer cylinder using a shear rate of 2096.0 s⁻¹, with a temperature control of ± 0.1 °C.

Fluorescence Anisotropy Studies. Fluorescence anisotropy measurements were collected on a Spex FluoroMax-2 steady-state spectrofluorometer, with a thermostated cell housing that allowed temperature control of ± 0.1 °C using a Julabo F20 circulating water bath. The apparatus is equipped with a polarization accessory, which uses the L-format instrumental configuration²⁵ and an automatic interchangeable wheel with Glan-Thompson polarizers. The steady-state fluorescence anisotropy values were determined as

$$r = \frac{I_V - GI_H}{I_V + 2GI_H} \quad (2)$$

where the subscripts of the fluorescence intensity values (I) refer to the orientation of the excitation and emission polarizers (V, vertical; H, horizontal). The instrumental correction factor G , which is the ratio of the sensitivities detection system for vertically and horizontally polarized light, is required for the L-format configuration and was automatically determined by the software supplied by the manufacturer. In all cases, the anisotropy values were averaged over an integration time of 20 s and a maximum number of three measurements for each sample. For the fluorescence anisotropy studies in micellar media, micellar solutions of C6 (1 μ M), RhB (2 μ M), and MC540 (2 μ M) with a total surfactant concentration of 25 mM were prepared. Fluorescence anisotropies were recorded using excitation and emission wavelengths of 465 and 505 nm for C6, 564 and 585 nm for MC540, and 554 and 574 nm for RhB. All anisotropy values in micellar media presented are the mean value of three individual determinations.

To obtain the calibration curves for the microviscosity determination, two solutions of C6 (1 μ M) and MC540 (2 μ M) in a 88.5 wt % EG–water binary mixture were prepared. The steady-state fluorescence anisotropy values in these solutions were recorded in the temperature range 5.2–50 °C using the same

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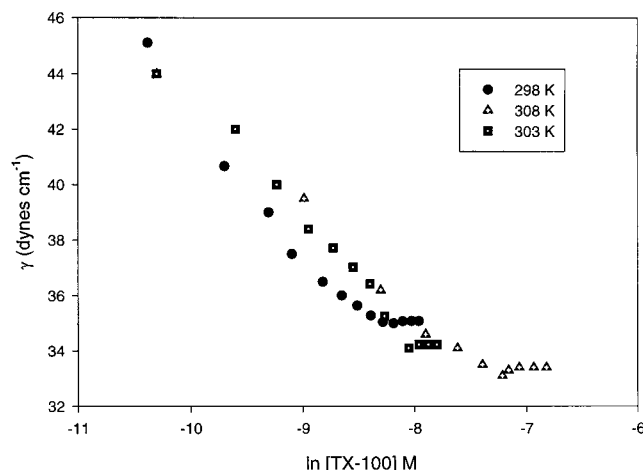


Figure 1. Surface tension of TX-100 as a function of \ln of surfactant concentration in 10 wt % EG solutions at different temperatures.

optical conditions as those employed in the case of the micellar media.

Results and Discussion

Determination of cmc and Thermodynamic Study.

Representative plots of the surface tension (γ) of a solution of TX-100 in a binary mixture of EG and water versus the bulk phase concentration are shown in Figure 1. There is a small dip in the surface tension near the intersection of the decreasing and the flat portions of the plot. The type of dip is thought to be due to traces of surface-active impurities or due to the composition distribution with a low degree of ethoxylation.²⁶ The dip was ignored in the determination of cmc values for TX-100. The cmc value was taken to be the point of intersection of the lines drawn through the two straight portions of the graph. The cmc values are in fair agreement with the published data in the literature.¹⁹ Slight differences can be attributed to the different methods employed for cmc determination (Table 1).

The surface excess concentration, Γ_{\max} , and the minimum area per surfactant molecule, A_{\min} , at the air/solvent interface were obtained using the surface tension measurements and the following equations:

$$\Gamma_{\max} = -\frac{1}{RT} \left[\frac{\partial \gamma}{\partial \ln C} \right]_{T,P} \quad (3)$$

$$A_{\min} = 1/N_A \Gamma_{\max} \quad (4)$$

where R is the gas constant, N_A is Avogadro's number, γ is the corrected surface tension value, and C is the concentration of surfactant in solution. The values of the surface pressure at the cmc, Π_{cmc} , were obtained employing the following equation:

$$\Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (5)$$

Thermodynamics of Micellization. The Gibbs free energy of micellization was calculated using the equation

$$\Delta G_{\text{mic}}^{\circ} = RT \ln X_{\text{cmc}} \quad (6)$$

where X_{cmc} is the mole fraction of surfactant at the cmc.

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Table 1. Values of cmc for Triton X-100 in Various Ethylene Glycol + Water Mixtures, at Different Temperatures

wt % EG	T (K)	cmc $\times 10^4$ (mol L ⁻¹) ^a	vol % EG	cmc $\times 10^4$ (mol L ⁻¹) ^b
0	298	2.38	0	2.40
0	303	2.31		
0	308	2.04		2.21
10	298	2.80	10	2.92
10	303	2.90		
10	308	3.08		3.10
15	298	3.53		
15	303	3.80		
15	308	3.92		
20	298	3.47	20	3.89
20	303	3.92		
20	308	3.94		4.54
30	298	5.60		
30	303	5.90		
30	308	6.47		
40	298	7.40	40	9.91
40	303	7.86		
40	308	8.57		12.1

^a Surface tension measurements. ^b Literature values (ref 19).

The enthalpies of micellization were obtained from the temperature variation of the cmc, by employing the equation

$$\Delta H_{\text{mic}}^{\circ} = -RT^2 \left(\frac{\partial \ln X_{\text{cmc}}}{\partial T} \right)_P \quad (7)$$

The entropy values of micelle formation were evaluated from the calculated enthalpy and free energy values as follows:

$$\Delta S_{\text{mic}}^{\circ} = (\Delta H_{\text{mic}}^{\circ} - \Delta G_{\text{mic}}^{\circ})/T \quad (8)$$

The effect of the cosolvent on the micelle aggregation process ($\Delta G_{\text{M}}^{\circ}$) was calculated from the following equation:

$$\Delta G_{\text{M}}^{\circ} = \Delta G_{\text{mic(EG+H}_2\text{O)}}^{\circ} - \Delta G_{\text{mic(H}_2\text{O)}}^{\circ} \quad (9)$$

The thermodynamic parameters of adsorption were obtained using the equation

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{mic}}^{\circ} - \Pi_{\text{cmc}}/\Gamma_{\max} \quad (10)$$

The standard state in the surface phase is defined as the surface covered with a monolayer of surface-active agent at a surface pressure equal to zero.

In pure water, the cmc values of the TX-100 were found to decrease with increasing temperature (Table 1). Within the temperature range employed in the present investigation, this behavior may be taken as a typical characteristic of nonionic surfactants.²⁷ It is well-known that London dispersion forces are the main attractive forces in the formation of the micelles and that micelle formation is supposed to be the result of hydrophobic interaction.^{28,29} In the case of nonionic surfactants, the decrease in cmc value with an increase in temperature is attributed to the dehydration of the poly(oxyethylene) moiety of the surfactant molecule.

In the presence of EG, the cmc values are increased considerably. The larger cmc value as the content of EG increases is a result of the presence of a structure-breaking

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Table 2. Thermodynamics of Micellization of TX-100 in Various Ethylene Glycol + Water Mixtures

wt % EG	<i>T</i> (K)	$\Delta G_{\text{mic}}^{\circ}$ (kJ mol ⁻¹)	$\Delta H_{\text{mic}}^{\circ}$ (kJ mol ⁻¹)	$\Delta S_{\text{mic}}^{\circ}$ (J K ⁻¹ mol ⁻¹)	$\Delta G_{\text{M}}^{\circ}$ (kJ mol ⁻¹)	$\Delta G_{\text{ads}}^{\circ}$ (kJ mol ⁻¹)
0	298	-30.6	11.4	141		-52.6
	303	-31.2	11.8	142		-53.6
	308	-32.1	12.2	144		-53.3
10	298	-30.1	-7.2	78	0.5	-55.4
	303	-30.5	-7.2	77	0.7	-61.9
	308	-30.9	-7.5	76	1.2	-67.0
20	298	-29.4	-9.8	66	1.2	-60.4
	303	-29.6	-10.2	64	1.6	-67.6
	308	-30.1	-10.5	64	2	-77.4
30	298	-28.0	-10.6	58	2.6	-61.3
	303	-28.4	-11.0	57	2.8	-79.1
	308	-28.8	-11.3	57	3.3	-90.9
40	298	-27.2	-12.1	50	3.4	-66.7
	303	-27.5	-12.5	49	3.7	-83.4
	308	-27.5	-12.9	47	4.6	-149.3

solute. The increase is larger than for ionic surfactants and can be attributed to the increase in solubilization of the nonpolar chain of the surfactant by EG. Structure-breaking solutes in the aqueous phase may disturb the hydrophobic group causing a decrease in the hydrophobic effect. The EG in the present study is acting as a cosolvent and a structure-breaking solute, decreasing the hydrophobic effect considered to be the driving force for micellization.¹¹⁻¹⁶ The increase in cmc values with temperature at a given concentration of EG is attributed to the disruption of the solvent structure with the increase in temperature.

As indicated by the negative values of the Gibbs energies of micellization, it is evident that as the content of EG increases the micellization process becomes less spontaneous (Table 2). The equation employed to calculate the Gibbs energy of micellization applies normally when the mean aggregation number is large³⁰ but may not be accurate for higher concentrations of cosolvent. The value obtained for the enthalpy and entropy of micellization must therefore be viewed only as an approximation. However, from the presented data some generalizations may be drawn.

In the absence of the additive, the free energy of micellization becomes more negative with an increase in temperature indicating that the formation of micelles becomes more spontaneous with increasing temperature. In the presence of additive, the variation is similar, even though the cmc values increase with temperature. This indicates that the change in the magnitude of the logarithm of the cmc term is more than compensated by the change in the values of the RT term.³¹

The enthalpy of micellization values in the presence of EG is negative and independent of temperature within experimental error. The enthalpy values calculated from eq 7 may differ from the directly measured calorimetric values;³² however, we were unable to locate any data for this system for comparison.

The entropy of micellization is positive in water and becomes less positive in the presence of increasing amounts of EG. In a pure water medium, the presence of hydrated oxyethylene groups of the surfactant introduces structure in the liquid water phase. Removal of the surfactant monomers due to micellization results in an overall increase in randomness and high entropy values. In the presence of the additive, the entropy changes are not as

Table 3. Surface Excess Concentration (Γ_{max}), Minimum Area per Molecule (A_{min}), and Surface Pressure at the cmc (Π_{cmc}) for TX-100 in Aqueous Mixtures of Ethylene Glycol

composition (wt % of EG)	<i>T</i> (K)	Γ_{max} (10 ⁶ /mol m ⁻²)	A_{min} (10 ²⁰ /m ²)	Π_{cmc} (mN m ⁻¹)
0	298	1.82	91	40.10
	303	1.90	87	42.63
	308	2.00	83	42.30
10	298	1.36	122	34.46
	303	1.17	142	36.72
	308	1.05	158	37.89
20	298	1.05	158	32.53
	303	0.79	211	30.00
	308	0.74	223	35.01
30	298	0.89	187	29.65
	303	0.59	280	29.90
	308	0.53	316	32.90
40	298	0.73	227	28.81
	303	0.51	323	28.51
	308	0.24	686	29.24

large as in pure water indicating that the additive lowers the energy of the three-dimensional water structure due to its structure-breaking ability.

The $\Delta G_{\text{M}}^{\circ}$ values that were found are positive in all cases. The positive values of $\Delta G_{\text{M}}^{\circ}$ can be understood on the basis of a reduction of the hydrophobic interactions caused by improved solvation. It is also possible to calculate the so-called enthalpy of transfer function similar to $\Delta G_{\text{M}}^{\circ}$ of transfer. The calculated values are found to be exothermic in all cases. It has been established that a hydrophilic group transfer from water to aqueous solution is exothermic and that of a hydrophobic group is endothermic.^{33,34} The overall exothermicity in the present study indicates that both the structure-breaking ability of EG and its interaction with the oxyethylene groups of the surfactants are dominating factors.

Thermodynamics of Adsorption. The values of surface excess increase with temperature in the absence of EG (Table 3). As the temperature increases, the hydration of the ethoxy segments of TX-100 is reduced and hence the tendency to locate at the air/water interface. In the presence of EG, the value of Γ_{max} decreases both with temperature and with increasing EG concentration (Table 3). This decrease can be attributed to several factors, namely, (a) a change in the water structure due to the addition of EG, (b) the interaction between the EG and the surfactant, and (c) the presence of the EG at the interface.³¹

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The effectiveness of a surface-active molecule is measured by the value of surface pressure, Π_{cmc} . At a particular concentration of additive, the values of Π_{cmc} were found to be slightly higher at high temperatures, indicating slightly more adsorption at the air/liquid interface at higher temperatures. It was also found that the surface activity of the TX-100 decreases slightly with increasing concentration of EG at a given temperature.

The $\Delta G_{\text{ads}}^{\circ}$ values are more negative than the corresponding $\Delta G_{\text{mic}}^{\circ}$ values. This indicates that when a micelle is formed, work has to be done to transfer the surfactant molecules in the monomeric state at the surface to the micelle through the aqueous media. The values of $\Delta G_{\text{ads}}^{\circ}$ become more negative with respect to temperature, implying that the dehydration of the hydrophilic group is a necessary condition for the adsorption to take place. At higher temperatures, the surfactant is less hydrated and requires less energy for the adsorption process.

Light Scattering Studies. The mean intensity of the light scattered by a solution of macromolecules contains information on the molecular weight of the macromolecules. On the other hand, the intensity of the scattered light continuously fluctuates around a mean value due to the Brownian movement of the macromolecules. The dynamic light scattering experiments make use of the fact that the time dependence of these fluctuations can be related to the translational diffusion coefficient of the macromolecules. To quantify this time dependence, one can fit the normalized autocorrelation function ($g^2(q, \tau)$) using a cumulants series expansion:

$$\ln[g^2(q, \tau) - 1]^{1/2} = (1/2) \ln \beta - \Gamma_1 \tau + \Gamma_2 \tau^2/2 + \dots \quad (11)$$

where τ is the delay time, q is the scattering wave vector, and β and Γ_1 are fitting parameters. The scattering wave vector is related to the scattering angle θ by $q = (4\pi n/\lambda) \sin(\theta/2)$, with n the refractive index of the solvent and λ the wavelength of light in vacuo. The parameter Γ_1 describes the diffusion of the particles under study. The collective diffusion coefficient (D_c) is related to Γ_1 by

$$D_c = \frac{\Gamma_1}{q^2} \quad (12)$$

The diffusion coefficient so measured by dynamic light scattering reflects the collective diffusion of the micelles or the diffusion of the micelles as affected by the intermicellar interactions. At elevated micelle concentrations, these interactions are of two types: direct interaction (such as repulsive excluded-volume effects and attractive van der Waals interactions) and hydrodynamic interactions (in which the motions of one particle are communicated to other particles via the flow of the solvent). According to the linear interaction theory,^{35,36} within the dilute region the collective diffusion coefficient varies linearly with the surfactant concentration, that is,

$$D_c = D_0[1 + k_D(c - \text{cmc})] \quad (13)$$

where D_0 is the diffusion coefficient in the absence of interaction, that is, at the cmc, k_D is a constant connected to the interparticle interaction potential, and c is the surfactant concentration.

Once the D_0 value is determined, the micellar hydrodynamic radius, R_h , may be obtained using the Stokes–

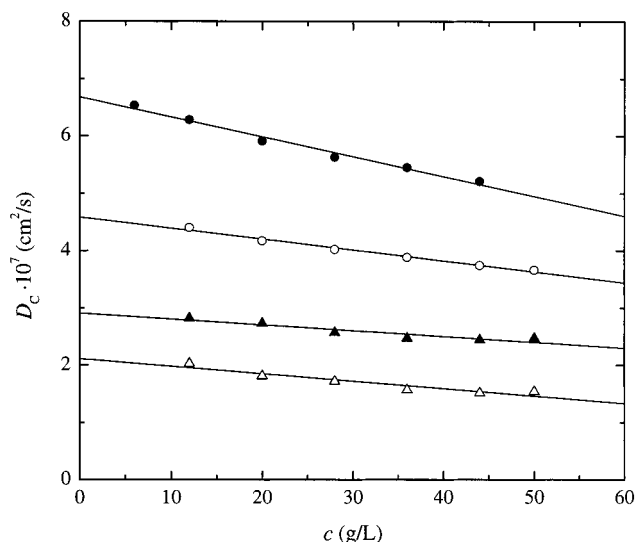


Figure 2. Diffusion coefficients vs TX-100 concentration at 25.0 °C in different EG–water mixed solvents: (●) water, (○) 20 wt % EG, (▲) 40 wt % EG, and (△) 60 wt % EG.

Table 4. Actual Diffusion Coefficients and Structural Parameters of TX-100 Micelles as a Function of Ethylene Glycol Content in the Mixed Solvent, at 25 °C

EG (wt %)	$D_0 \times 10^7$ (cm ² /s)	R_h (nm)	M_w (Da)	N_{agg}	R_0 (nm)	a_0 (Å ²)
0	6.63	3.7	65 500	105	2.9	100.7
20	4.58	3.6	53 000	85	2.7	107.8
40	2.91	3.1	25 200	40	2.1	138.5
60	2.11	2.5	20 200	32	1.9	141.8

Einstein relation as given by

$$D_0 = \frac{k_B T}{6\pi\eta_0 R_h} \quad (14)$$

where $k_B T$ has its usual meaning and η_0 is the solvent viscosity.

To facilitate the light scattering measurements, we performed the experiments at surfactant concentrations ranging from 10 to 50 g/L. These surfactant concentrations are high enough to permit the measurements of the micellar size. Figure 2 presents the determined D_c values versus surfactant concentration in water and EG–water solutions. The cmc value is quite small, and within the experimental error, the concentration of the surfactant is taken to be equal to the total surfactant concentration.

As can be seen in Figure 2, the apparent diffusion coefficient is a decreasing function of the surfactant concentration. The experimental data are linear ($r > 0.99$), in qualitative agreement with eq 13, with slightly different slopes and different intercepts. The collective diffusion coefficients show a weak dependence on the surfactant concentration as expected for neutral surfactants where the intermicellar interactions are weak. The actual diffusion coefficient, D_0 , was obtained by extrapolation of the data to zero concentration. From the value of D_0 , the hydrodynamic radii, R_h , were calculated according to eq 14. The values of D_0 and R_h are listed in Table 4. The experimental results indicate a large reduction in D_0 with increasing EG concentration. At least part of this change in D_0 is attributed to the increase in solvent viscosity. For example, the viscosity of 60% EG is almost 5 times the viscosity of water at the same temperature. From Table 4, there is a substantial and progressive decrease in the hydrodynamic micelle radius with increasing EG content.

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This can be due to a decrease in the aggregation number and/or a decrease in micellar solvation. To resolve this question, we combined the dynamic and the static light scattering measurements to yield the values of the micelle hydrodynamic radius and the aggregation numbers.

The intensity of scattered light depends both on the molecular weight of the micelles and on the intermicellar interactions. Under certain circumstances, the intermicellar interactions can be neglected and the molecular weight of the micelles can be determined by static light scattering. In these experiments, the Rayleigh ratio of the sample solutions is determined using toluene as a standard according to the relationship

$$R_\theta = \frac{I_\theta}{I_{\text{tol}}} R_{\text{tol}} \quad (15)$$

where I_θ and I_{tol} are the scattered intensity of the sample solution and the toluene, respectively, and R_{tol} is the Rayleigh ratio of toluene. For R_{tol} at $\lambda = 488$ nm, a value of $31.6 \times 10^{-4} \text{ m}^{-1}$ was assumed.³⁷ In general, the difference in the Rayleigh ratio between the micellar solution and the solvent solution in the absence of micelles, $\Delta R_\theta = R_\theta - R_\theta^0$, as determined by static light scattering is given by the expression

$$\Delta R_\theta = K(c - \text{cmc}) M_w P(q) S(q, c) \quad (16)$$

where M_w is the molecular mass of the micelles, $P(q)$ is the micelle form factor, $S(q)$ is the structure factor, and K is an optical constant given by

$$K = \frac{4\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda_0^4} \quad (17)$$

where n_0 is the solvent refractive index, dn/dc is the refractive index increment of the sample solution, and λ_0 is the wavelength of incident light in a vacuum. The particle form factor describes the intramicelle interference and essentially describes the angular dependence of the scattering intensity. It is usually expressed in terms of the scattering wave vector, q . If the particle size is much smaller than the wavelength of light, as we expect for the micelles formed by TX-100 surfactant, then the scattering intensity generally shows a very low angle dependence, and the contribution of $P(q)$ can be neglected, that is, $P(q) = 1$.³⁸

On the other hand, the structure factor reflects the intermicellar interaction and it is dependent on the interaction potential on the basis of the theory of simple liquid.³⁹ The $S(q)$ value oscillates and is damped around unity as a function of q , being equal to unity when interactions are negligible. In this case, the intensity of the scattered light can be directly related to the molecular weight of the micelles, by^{40,41}

$$\frac{K(c - \text{cmc})}{\Delta R_\theta} = \frac{1}{M_w} \quad (18)$$

In this equation, c is the total surfactant concentration,

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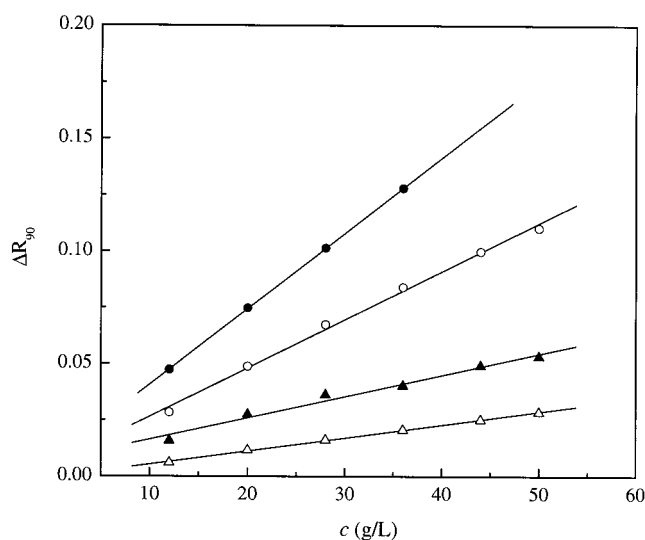


Figure 3. The excess of scattering (ΔR_{90}) as a function of TX-100 concentration at 25.0 °C in various media with different EG content. Symbols are as in Figure 2.

but for all the micellar solutions examined, $c \gg \text{cmc}$, so that the micelle concentration $c - \text{cmc} \approx c$. Experimentally, we determined M_w for each sample by measuring $Kc/\Delta R_\theta$ and applying eq 18.

Equation 18 can be used in the case of a nonionic surfactant at relatively low surfactant concentrations.^{42,43} These micelles are not charged and therefore do not exhibit strong electrostatic interactions, and the surfactant concentration is low enough that repulsive, excluded-volume interactions, and attractive interactions can be neglected. Conversely, if the micelle size does not change with increasing surfactant concentration, as in the case of a pure nonionic surfactant in aqueous solution,⁴⁴ the micelle size can be determined by extrapolating the static light scattering data to the cmc, where the intermicellar interactions are negligible. The micelles can be seen as individual aggregates that are diffusing almost independently of each other.

Note that in eq 16 the Rayleigh ratio depends on the scattering angle. However, in the present systems ΔR_θ did not exhibit a strong angular dependence, and hence ΔR_θ may be replaced with the ΔR_θ when $\theta = 90^\circ$. Figure 3 shows the Rayleigh ratio versus micellar concentration in four media (0%, 20%, 40%, and 60% EG content). Linear regression analysis of the data was used to estimate the slopes, which give the micellar molecular weights (M_w). The good linearity ($r > 0.999$) obtained in the present study indicates that the intermicellar interactions are minimal. Also, the micellar molecular weights are essentially independent of c in the present range of surfactant concentrations.

From M_w , we obtained the aggregation number values, N_{agg} , and hence the dry micellar volumes, V_0 , by

$$V_0 = \frac{v M_w}{N_A} \quad (19)$$

By assuming a spherical geometry for TX-100 micelles, we estimated the micellar radii (R_0). The values obtained

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for M_w , N_{agg} , and R_0 are listed in Table 4. The value of the micellar aggregation number in water is in excellent agreement with literature values.^{45–48} Data in Table 4 show that the aggregation number of TX-100 micelles decreases by around 70% when the solvent contains 60% EG, whereas the corresponding hydrodynamic volume (estimated from the hydrodynamic radius) is reduced by approximately 69%. This fact indicates that micellar solvation is not substantially modified in magnitude with EG addition, and therefore the decrease of the micellar size is mainly due to the reduction of the aggregation number. In regard to the obtained trend in the dependence of N_{agg} on EG content, a similar behavior has been observed by Cantú et al.²⁰ for monododecyl octaethylene glycol in water–glycerol mixtures by using light scattering measurements. However, Penfold and co-workers²² have observed an opposite trend for monododecyl octaethylene glycol and monododecyl hexaethylene glycol in water–glycerol and water–EG mixtures, respectively. In this study, the experimental data, obtained by the SANS technique, were analyzed under a model with four fitting parameters, one of them being the micellar aggregation number. At the present time, it is difficult to justify these contradictory results, which could be related to the different experimental methods employed.

We have also included in Table 4 the surface area per headgroup, a_0 , as determined from the dry radius and the aggregation number by assuming a spherical geometry. The surface area per headgroup is an important structural parameter that plays a decisive role in the geometric or packing properties of micelles,⁴⁹ controlling the magnitude of the steric repulsions between the heads.⁵⁰ As can be seen in Table 4, the surface area per headgroup of TX-100 increases with the presence of EG in the solvent mixture. This behavior can be rationalized if we assume that EG takes part in the solvation layer of the micelles, by replacing some of the water molecules. In this way, as an EG molecule is approximately 3.1 times larger than a water molecule, substitution of several water molecules by the former will result in a thicker solvation layer. As a consequence, the steric repulsions between micelles would be increased as the EG content increases in the solvent system. In addition, the increase of a_0 would impede the growth of the micelles, forcing them to adopt spherical shapes.

Fluorescence Anisotropy Studies. It is assumed that solvation plays a fundamental role in the configuration of the oxyethylene chain of nonionic surfactants. This interaction is decisive in the surfactant monomer packing into the micelle.⁵¹ The data from the preceding section indicate that the nature of the solvation layer is altered by EG addition. The formation of a thicker solvation layer must be accompanied by an increase in the local rigidity of this micellar region. To test this hypothesis, we carried out fluorescence polarization measurements using a number of fluorescent probes. The steady-state anisotropy (r) is related to the viscosity around the probe (η) by Perrin's equation

$$\frac{1}{r} = \frac{1}{r_0} + \frac{k_B T \tau}{r_0 V \eta} \quad (20)$$

where r_0 is the limiting anisotropy obtained in the absence

of rotational motion, k_B is the Boltzmann constant, T is the absolute temperature, and V and τ are the molecular volume and fluorescence lifetime of the probe, respectively. Accordingly, polarized emission measurements can provide information on the local viscosity around the probe, the so-called microviscosity. It must be pointed out that the microviscosity concept has been criticized. This is because a number of assumptions inherent to the application of this method have been demonstrated to be unjustified.^{52,53} Usually, two problems are raised in this respect: (a) different probes, often residing in different regions of the micelle, report different microviscosity values and (b) micelle rotation may contribute to the depolarization of some probes located in micelles. However, the usefulness of this parameter in investigations involving a series of homologous surfactants having similar chemical structures has also been demonstrated.⁵⁴ In these cases, changes in the micellar microviscosity can reveal relative modifications in the microstructure of the micelle. Therefore, the microviscosity values reported in this paper should be considered in this context, that is, as relative variations of the microstructure of TX-100 micelles based on the solvent composition, rather than as absolute terms.

We selected three different fluorescence probes with different characteristics and hence different ways of associating with TX-100 micelles. First, to obtain information on the structural changes in the micellar interior, we performed fluorescence anisotropy studies with C6. This is an uncharged laser dye, essentially insoluble in water, whose photophysical properties in homogeneous and micellar media have been reported.⁵⁵ From its spectral behavior in different solvents, it can be inferred that this probe is solubilized in the palisade layer of TX-100 micelles, where it senses a relative polar microenvironment similar to that of ethanol. On the other hand, to gain information about changes in the micellar surface we used two charged probes, RhB and MC540. It has been reported that some cationic dyes, like RhB, can interact with TX-100 through a charge-transfer mechanism, where TX-100 acts as the electron donor and the dye acts as the electron acceptor.⁵⁶ MC540 is an anionic lipophilic dye, and its spectroscopic properties in both homogeneous and micellar media have been well studied.^{57–60} Ionic lipophilic probes tend to be located near the micellar surface, with their polar part directed toward the water–micelle interface whereas the nonpolar portion is oriented toward the hydrophobic region of the micelle. In fact, it has been reported⁵⁹ that MC540 is anchored to nonionic micelles, such as TX-100, through hydrophobic interactions of the tetramethylenic tails that become embedded in the interior of the micelle.

To obtain a quantitative estimation on microviscosity

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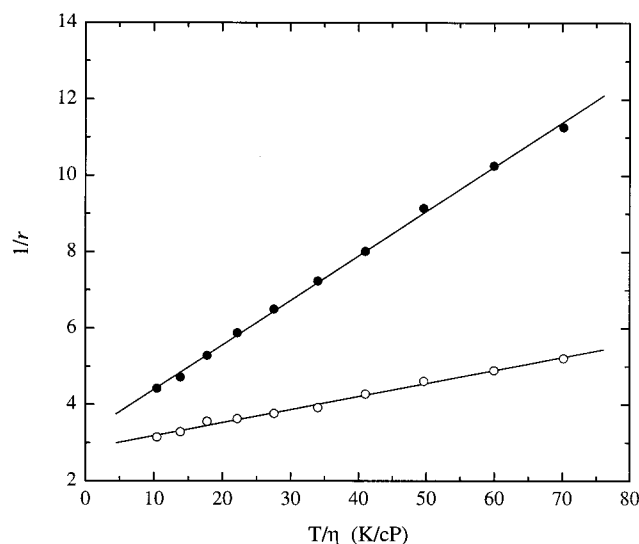


Figure 4. Calibration curve for coumarin 6 (●) and merocyanine 540 (○) in EG–water (88.5 wt %) mixed solutions. Data are plotted according to the Perrin equation.

changes of TX-100 micelles, calibration curves for C6 and MC540 were prepared. A temperature dependence study with both probes in 88.5 wt % EG solutions was carried out, and the results of these experiments, plotted according to Perrin's equation, are shown in Figure 4. As can be seen, in both cases a good linear correlation was found. From the calibration curves in Figure 4, we obtained the limiting anisotropy (r_0) values for C6 (0.310) and MC540 (0.352), in good agreement with literature values.^{55,59} In addition, it is also observed that the slope of the C6 line is greater than that of the MC540, indicating that the former shows a greater sensitivity to viscosity changes.

In Figure 5, the results obtained for the fluorescence anisotropy of C6 and MC540 in TX-100 micelles are presented as a function of the EG concentration. Both probes show an increase of anisotropy, higher in the case of C6, and reach a plateau value at approximately 35 wt % EG. Moreover, since the local polarity or micropolarity is an important property that can reveal structural changes in micelles, we also measured the change of micropolarity of TX-100 micelles as a function of EG addition. The pyrene 1:3 ratio index was used in this case. This parameter is well-known to be a sensitive indicator of the palisade layer polarity, where the pyrene is preferentially solubilized.^{61,62} The results of these measurements have been included in Figure 5a. Interestingly, the pyrene 1:3 ratio also shows a definite change at about 35 wt % EG, in this case the onset of a steady rise. However, the observed increase in the pyrene 1:3 ratio index is not necessarily due to an increase of micropolarity. It is also possible that the increase of the surface area per headgroup forces the probe to be located further outward in the micelle, where the polarity sensed by the probe would increase. In any case, it is clear that the behavior of the pyrene 1:3 ratio reflects a significant structural change in the TX-100 micelles induced by the EG addition, as do the C6 and MC540 measurements.

In Table 5, the microviscosity values as determined from the calibration curve in Figure 4 for C6 and MC540 are listed. Data in Table 5 indicate that the addition of EG to the solvent system induces an increase of the micro-

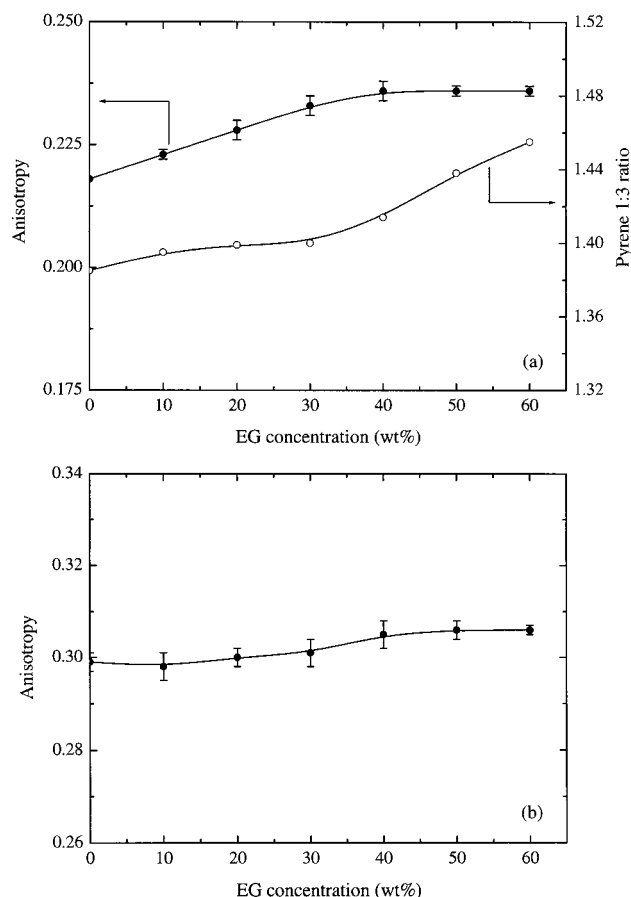


Figure 5. Fluorescence anisotropy (●) of coumarin 6 (a) and merocyanine 540 (b) together with the pyrene 1:3 ratio (○) in TX-100 micellar solutions (25 mM) as a function of EG solvent content, at 25 °C.

Table 5. Fluorescence Anisotropy, r , for Coumarin 6 (C6) and Merocyanine 540 (MC540) and the Corresponding Microviscosity Values, η , in TX-100 Micellar Solutions with Different Ethylene Glycol Concentrations, at 25 °C

EG (wt %)	C6		MC540	
	r^a	η (cP)	r^a	η (cP)
0	0.218	26.2	0.299	20.1
10	0.223	28.2	0.298	19.6
20	0.228	30.7	0.300	20.5
30	0.233	33.4	0.301	21.0
40	0.236	35.2	0.305	23.1
50	0.236	35.2	0.306	23.7
60	0.236	35.2	0.306	23.7

^a Mean value of three individual determinations.

viscosity in both the palisade layer and the surface of TX-100 micelles. In addition, it is also observed that the relative variation of microviscosity reported by MC540 is smaller than in the case of C6. Two reasons could be given for this: first, C6 is more sensible to changes of viscosity, as seen from data in Figure 4; second, it is possible that the probable participation of EG in the solvation layer causes the transfer of some MC540 molecules from the micellar surface to the bulk solution. Therefore, the data in Table 5 at high EG content, in the case of MC540, would be underestimated and, consequently, the effect produced by the EG addition would be larger than that reflected by our results. Moreover, it is important to point out that fluorescence depolarization of probes associated with micelles can be caused by either (a) rotation of the probe in the micelle or (b) rotation of the micelle itself. Addition of the EG can affect the above process in two opposing

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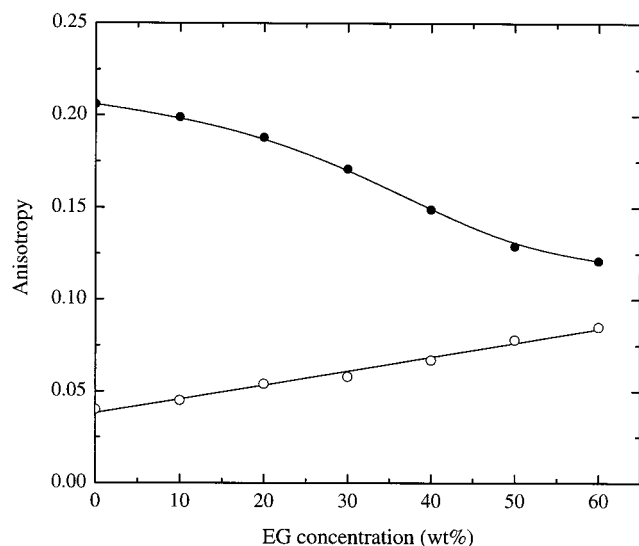


Figure 6. Fluorescence anisotropy of rhodamine B in 25 mM TX-100 micellar solutions (●) and in homogeneous media (○) as a function of EG solvent content, at 25 °C.

ways. On one hand, as the micellar size becomes smaller with the EG addition, the micellar rotation should increase. On the other hand, the cosolvent addition produces an increase in the viscosity of the medium, retarding this second rotational process. Although we cannot determine the quantitative contribution of these effects, it seems reasonable to attribute the increase of the microviscosity values to a structural modification in the solvation layer of TX-100 micelles, induced by the EG addition. This picture is consistent with a certain participation of EG in the solvation of the headgroups of the surfactant, as discussed above.

Finally, Figure 6 shows the fluorescence anisotropy values of RhB in both homogeneous and micellar media as a function of the EG concentration. Data in the homogeneous medium indicate that the anisotropy of RhB increases with the EG concentration and, consequently, with the viscosity. However, a continuous decrease is observed in the micellar medium. This behavior clearly indicates that the addition of EG produces desolvation of RhB bound to TX-100 micelles, and some molecule probes are removed from the micellar surface and transferred to the bulk. In the case of RhB, the magnitude of this effect is considerably larger than for MC540. This is probably due to the different association mechanisms of the probes to the TX-100 micellar surface. Whereas MC540 is strongly bound to the micellar surface of TX-100,⁵⁹ RhB is only partially micellized in TX-100, residing about 50% in the bulk phase.⁶³ It is important to point out that although we cannot extract conclusions about changes of microviscosity at the micellar surface from the RhB data, it must be recognized that its behavior is also consistent with our hypothesis of a certain participation of EG in the micellar solvation layer.

Cloud Points. Nonionic surfactant solutions show a complex phase behavior. Their most characteristic feature is that a liquid–liquid phase separation occurs when the temperature rises above a certain value. This phenomenon gives rise to turbidity in the solution, and the temperature at which the incipient phase separation occurs is the cloud point.^{64,65} It is widely assumed that the phase separation

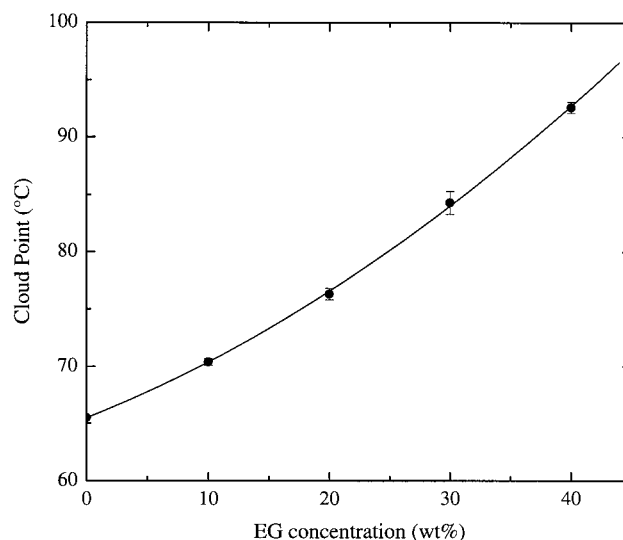


Figure 7. Variation of the cloud point of TX-100 (25 mM) with the EG content in the solvent system.

is due to the reduction of the intermicellar repulsions, as a result of the dehydration of the oxyethylene groups as the temperature is increased. Since we observed that the addition of EG produces a remarkable alteration in the solvation layer, it seems interesting to evaluate and to analyze its influence on the cloud point of the TX-100 micellar solutions. Therefore, we measured the cloud point of TX-100 at three different concentrations (12.5, 25, and 50 mM) as a function of the EG added. Since only small changes were found to occur in the surfactant concentration range studied, the results obtained for 25 mM TX-100 are presented as representative in Figure 7. In the figure, it can be seen that the addition of EG produces an increase in the cloud point. A similar effect has been reported by Penfold et al.²² for monododecyl hexaethylene glycol in water/EG mixtures. However, the opposite behavior has been observed in the case of water/glycerol mixtures.^{20,22} The aforementioned authors did not observe experimental evidence for the participation of EG in the micellar solvation layer and attributed the rise of the cloud point to an increased compatibility between the solvent and surfactant headgroup. The authors did not propose a mechanism involving this compatibility. We postulate that the influence of EG on the cloud point of TX-100 can be rationalized on the basis of two essential effects: (a) an increase of the repulsive steric interactions between the solvated micelles and (b) a decrease of the attractive van der Waals interactions due to the reduction of the dielectric constant of the medium. Note that according to our hypothesis, if the solvated micelle is modified by the participation of some EG molecules, the resulting effect would be the formation of a thicker solvation layer, which would increase the steric repulsions between micelles in the presence of EG at a fixed temperature. An increase of temperature at a fixed EG concentration will produce the desolvation of the oxyethylene chains and, as a consequence, a reduction of the steric repulsions between micelles. This will facilitate the formation of large particles and the appearance of turbidity in the solution. Therefore, larger EG concentrations will require a greater rise of temperature.

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Conclusions

We have performed a systematic study of the effect of EG on cmc, micellar size, microenvironmental properties, and cloud point of TX-100. Through a surface tension study in a temperature range, we have obtained the change of the cmc with EG addition. This study allows us to obtain both the thermodynamic parameters of micellization and of adsorption in the liquid–air interface. From these data, it could be deduced that the micellization process of TX-100 in the mixed solvent system is mainly controlled by two factors, namely, the structure-breaking ability of EG and the interaction of the cosolvent with the poly-(oxyethylene) groups of the surfactant. The surface activity of TX-100, as evaluated by the thermodynamic parameters of adsorption, was found to decrease with EG addition at a fixed temperature. The structural evolution of the aggregates formed in these media was examined by means of a combined analysis of static and dynamic light scattering measurements. When water was replaced with EG, the dynamic light scattering data indicated a reduction in the hydrodynamic radius of TX-100 micelles. The static light scattering measurements revealed that this reduction is attributable to a decrease in the aggregation number

rather than to a change in the whole micellar solvation. On the other hand, the observed trend of the surface area per headgroup of TX-100 suggested an increasing participation of EG molecules in the micellar solvation layer. From the fluorescence polarization assays, it could be deduced that EG addition in the solvent system causes an increase in the micellar microviscosity. This effect was attributed to a certain participation of EG in the solvation layer of the micelle. Finally, the cloud point of the surfactant was found to increase on EG addition. This tendency was discussed on the basis of two effects: the formation of a thicker solvation layer, consistent with the mentioned change of microviscosity, and a reduction of the dielectric constant of the medium, producing the depression of the attractive van der Waals interactions.

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