Micellization of Poly(ethylene oxide)–Poly(propylene oxide)–Poly(ethylene oxide) Triblock Copolymers in Aqueous Solutions: Thermodynamics of Copolymer Association

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ABSTRACT: The critical micellization temperature (cmt) and critical micellization concentration (cmc) values of 12 Pluronic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymers, covering a wide range of molecular weights (2900–14 600) and PPO/PEO ratios (0.19–1.79), were determined employing a dye solubilization method. A closed association model was found to describe adequately the copolymer micellization process for the majority of the Pluronics and used to obtain the standard free energies ($\Delta G°$), enthalpies ($\Delta H°$), and entropies ($\Delta S°$) of micellization. It was determined that the micellization process is entropy-driven and has an endothermic micellization enthalpy. The hydrophobic part of the Pluronics, PPO, was responsible for the micellization, apparently due to diminishing hydrogen bonding between water and PPO with increasing temperature. The cmc dependence on temperature and size of headgroup (PEO) of Pluronics follows a similar trend with lower molecular weight C_iE_j nonionic surfactants, the effect of temperature being more pronounced with the Pluronics. The PEO–PPO–PEO block copolymers were compared to PPO–PEO–PPO block and PEO–PPO random copolymers, in an attempt to probe the effect of molecular architecture in the formation of micelles. No micelles were observed in aqueous PPO–PEO–PPO block copolymer solutions with increasing temperature, up to the cloud point.

Introduction

Water-soluble triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), often denoted PEO–PPO–PEO or $(EO)_{m1}(PO)_n(EO)_{m2}$, are commercially available nonionic macromolecular surface active agents. Variation of the molecular characteristics (PPO/PEO ratio, molecular weight) of the copolymer during the synthesis allows the production of molecules with optimum properties that meet the specific requirements in different areas. As a result, PEO–PPO–PEO block copolymers are an important class of surfactants and find widespread industrial applications in detergency, dispersion stabilization, foaming, emulsification, lubrication, etc.,[1,2] along with more specialized applications in, e.g., pharmaceutics (drug solubilization and controlled release[3-6]), bioprocessing (protecting microorganisms against mechanical damage[7]), and separations (solubilization of organics in aqueous solutions[8,9]). Commercial names for these surfactants are Poloxamers (ICI) and Pluronics (BASF).

Temperature-dependent micellization and gel formation are two of the most characteristic properties of aqueous PEO–PPO–PEO block copolymer solutions. Owing to the marked change in water solubility of the center poly(propylene oxide) block at elevated temperatures, the block copolymers form various aggregates, depending on the degree of polymerization ($m1$, $m2$, and n). A number of triblock copolymers have been shown to aggregate in the form of micelles,[10-15] with a core presumably dominated by PPO and a corona dominated by hydrated PEO blocks.[16] It is also known that, at temperatures close to ambient, high-concentration copolymer solutions exhibit a dramatic change in viscosity, revealing a "thermoreversible gelation".[11,13,17,18] Several mechanisms have been proposed as driving forces for this thermal gelation: Rassing and Attwood[19] related the gel transition to intrinsic changes in the micellar properties and Vadnere et al.[20] discussed the gelation in terms of entropic changes involving locally ordered water molecules close to the hydrophobic units, whereas Wanka et al.[11] and Wang and Johnston[18] speculated at the possibility of an ordered three-dimensional structured state or network. Recently, neutron-scattering studies showed that the observed change in viscosity is due to a "hard-sphere crystallization" as the micelle concentration approaches the critical volume fraction of 0.53.[15] The critical micellization concentration (cmc), the fraction of polymer molecules in micellar form, and the size and the aggregation number of the micelles, as well as the temperature dependence of these parameters, are of great interest for aqueous PEO–PPO–PEO block copolymer micellar solutions. Starting with the average aggregation number, it has been shown by refs 10 and 15, using static light scattering and fluorescence quenching, that this increases with temperature; the absolute values, nevertheless, vary between different systems and even between different copolymer batches. Furthermore, the size of the micelles generally increases with increasing temperature, the extent of the increase varying between different copolymers; indeed for some systems the micelle hydrodynamic size remains constant while the aggregation number increases with temperature, probably a result of dehydration of the PEO headgroups.[10]

Perhaps the parameter of greatest fundamental value is the critical micellization concentration, the copolymer concentration at which micelles start forming.[21] As we show below, and as has previously been observed, the cmc of aqueous PEO–PPO–PEO block copolymer solutions decreases with increasing temperature.[10,12,13] In comparison with conventional, low molecular weight amphiphiles, there is some inherent complexity in the micellization of block copolymers, which depends strongly on their composition. The composition polydispersity could be appreciable even for a copolymer with a narrow distribution of molecular weight, and accordingly, no sharp cmc or cmt

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(critical micellization temperature, the copolymer solution temperature at which micelles form) has been observed for block copolymers. In practice, a certain cmc range with some notable uncertainty could be detected. A large difference is often noted between the cmc values determined by different methods because their sensitivity to the quantity of molecularly dispersed copolymers (unimers) present may vary.[10] For common detergents, a considerable amount of cmc data have been collected and summarized by Mukerjee and Mysels,[22] whereas for block copolymers so far only scarce cmc data (e.g., refs 23 and 24) are available in the literature. Furthermore, the values reported in the literature differ substantially; the lack of sufficient temperature control, in conjunction with batch-to-batch variations, may be responsible for the observed variations.[25]

The need for a systematic study of the cmc and cmt for the PEO–PPO–PEO block copolymers becomes apparent from the discussion in the preceding paragraph, both from an applications point of view (mapping the micellization/solubilization regime for a given copolymer) and from theoretical considerations (determining the origin of micellization and the effects of hydrophilic PEO and hydrophobic PPO). Furthermore, the thermodynamic parameters of copolymer micellization can be derived from cmc data at different temperatures, given a copolymer association mechanism,[26,27] providing further insight on the energetics of the micellization.

In a recent study that explored the potential for using PEO–PPO–PEO block copolymer micelles in the treatment of water contaminated with polycyclic aromatic hydrocarbons, it was shown that solubilization efficiency depended strongly on the molecular structure, composition, and molecular weight of the copolymer used.[9] Some speculation was made as to the reasons for this behavior, but verification of these arguments, which requires either structural experimental characterization or detailed theoretical analysis of the association and solubilization behavior of these polymer systems, is still lacking. In an attempt to address this issue, we undertook a detailed theoretical (using a self-consistent mean-field theory[28]) and experimental investigation on the micellization and solubilization in the aqueous PEO–PPO–PEO block copolymer solutions. We report here experimental results on block copolymer micelle formation and micellization thermodynamics.

The solubilization of a dye (1,6-diphenyl-1,3,5-hexatriene, DPH) in copolymer solutions, detected by its fluorescence and UV–visible spectra, was employed in our investigation for the determination of the solution cmt and cmc values. Spectroscopic techniques, based either on optical absorption or on emission of light from some "probe" molecule, are now well established for investigating a wide range of physical properties of micellar solutions.[29,30] The fact that micelles can solubilize relatively large amounts of sparingly water-soluble compounds has been used to determine the onset of micelle formation,[22,31] by measuring the concentration of a chosen sparingly soluble substance, possessing a convenient UV–visible absorbing chromophore, in the presence of increasing amounts of surfactant. Below the cmc, the concentration of the solubilizate in solution is the same as in aqueous solution in the absence of surfactant. Above the cmc, the total amount of the additive in solution increases sharply as the total micelle concentration increases. Chattopadhyay and London used fluorescence from DPH to determine the cmc of various surfactants,[32] obtaining values that were within 10% of the ones determined by other methods. Surface tension results showed that probe molecules, at the levels used to determine the cmc by fluorescence ($<10^{-6}$ kmol m^{-3}), did not noticeably affect the surfactant properties, viz., surface tension, nor the surface tension derived cmc value.[33] Edwards et al.[34] reported that, in general, the cmc values they obtained from the surface tension data for solutions of deionized water and nonionic surfactants showed fairly close agreement to the cmc values inferred from polyaromatic hydrocarbon solubilization data. Similar values for the cmc of the PEO–PPO–PEO block copolymers measured by surface tension and dye solubilization methods have been reported by Schmolka and Raymond.[35] The following are an example: L64 cmc value at 25 °C is 0.0016 g/dL or 5.6 μM (measured with dye absorption) and 4.2 μM (measured with surface tension); cmc value at 40 °C is 0.0033 g/dL or 11.5 μM (measured with dye absorption) and 13.9 μM (measured with surface tension).[35] However, different values for the cmc of the PEO–PPO–PEO block copolymers measured by surface tension and dye (benzopurpurine) solubilization methods have been reported by Anderson.[36] It becomes apparent though, from a closer inspection of his data, that Anderson misinterpreted the dye solubilization vs copolymer concentration curve. Such a curve is usually sigmoidal, with the first inflection indicating the micelle formation and the second inflection the complete solubilization of the dye. Anderson based his conclusions on the second inflection; the cmc value obtained from the first inflection of the dye solubilization vs copolymer (F68) concentration curve is actually very close to the cmc value derived from his surface tension measurements ($\sim 2 \times 10^{-3}\%$).

Table 1. Properties of the Pluronic Copolymers Used in This Study

polymer	MW	PPO segm wt	PO units	EO units	lot no.
L64	2 900	1740	30	2 × 13	WPWN-505A
P65	3 400	1700	29	2 × 18	WPAN-605B
F68	8 400	1680	29	2 × 76	WPON-611B
P84	4 200	2520	43	2 × 19	WPTN-561B
P85	4 600	2300	40	2 × 26	WPAN-628B
F88	11 400	2280	39	2 × 103	WPDN-616B
P103	4 950	3465	60	2 × 17	WPHM-539B
P104	5 900	3540	61	2 × 27	WPAN-503B
P105	6 500	3250	56	2 × 37	WPDI-522A
F108	14 600	2920	50	2 × 132	WPDN-564B
P123	5 750	4025	69	2 × 19	WPYM-569B
F127	12 600	3780	65	2 × 100	WPON-593B
25R4	3 600	2500	2 × 21	25	WPMN-515B

We measured the cmt and cmc values of 12 Pluronic PEO–PPO–PEO block copolymers, covering a wide range of molecular weights (2900–14 600) and PPO/PEO ratios (0.19–1.79). A closed association model was found to describe adequately the copolymer micellization process for the majority of the Pluronics. Using such a model, we obtained the standard free energies ($\Delta G°$), enthalpies ($\Delta H°$), and entropies ($\Delta S°$) of micellization and correlated them to the copolymer molecular weight and composition. We also compared the PEO–PPO–PEO block copolymers to PPO–PEO–PPO block and PEO–PPO random copolymers, in an attempt to probe the effect of molecular architecture on the formation of micelles.

Materials and Methods

Copolymers. The Pluronic PEO–PPO–PEO block copolymers were obtained from BASF Corp., Parsippany, NJ, and used as received. These polymers are available in a range of molecular weights and PPO/PEO ratios.[1,2,37] Table 1 lists the physical properties of the polymers studied (data supplied by the manufacturer). To facilitate analysis of the results, a brief description of the system of nomenclature for the BASF Pluronics follows. The notation for the Pluronic triblock copolymers starts with the letters L (for liquid), P (for paste), or F (for flakes). The first two numbers are indicative of the molecular weight of the PPO block, and the last number signifies the weight fraction of the PEO block. For example, P103 and P104 have the same molecular weight of PPO (on the order of 3000) but P103 has 30 wt % and P104 40 wt % PEO. The random PEO/PPO copolymer, UCON 50HB-3520 (50% PEO, 3520 molecular weight), was purchased from Union Carbide Chemicals and Plastics Company Inc., South Charleston, WV; the PPO-PEO-PPO Pluronic-R block copolymer, 25R4 (40% PEO), was obtained from BASF Corp.

Spectroscopic Probe. 1,6-Diphenyl-1,3,5-hexatriene (DPH) was obtained from Molecular Probes Inc., Eugene, OR, and used as received. The DPH dye used for the determination of the cmt and cmc in the present study is a well-known probe of membrane interiors. The primary application of DPH has been to estimate membrane "fluidity", based on fluorescence depolarization measurements.[38] Solvent and temperature effects on the fluorescence of DPH have been studied by Cehelnic et al.[39] The fluorescence of DPH is minimal in water and is substantially enhanced by association with lipids and other surfactants. This property has been exploited to determine the cmc's of anionic, uncharged, zwitterionic, and cationic detergents.[32] DPH has also been used in probing micelles of tetradecyltrialkylammonium bromides[40] and didodecyldimethylammonium bromide (DDAB)/alkane/water microemulsions.[41]

Sample Preparation. Aqueous copolymer solutions were prepared by dissolving the polymer in Milli-Q water (18 $M\Omega$ cm) and diluting to the desired concentration (ranging from 0.001% to 20% w/v). The experiments on the Pluronic solutions were performed within a few days of the solution preparation. A dye solubilization technique[32] was employed to determine the onset of copolymer micellization (cmc, cmt). Sample preparation was similar to that of Chattopadhyay and London:[32] a stock solution of 0.4 mM DPH in methanol was prepared; 25 μL (measured with a Hamilton microsyringe) of the DPH/methanol solution was added to 2.5 mL of copolymer solution, so that the final copolymer solution contained 1% v/v methanol and 0.004 mM DPH. The solutions were left in the dark to equilibrate for at least 3 h (and no more than 24 h) before the spectroscopic measurement. A single DPH concentration was used (0.004 mM), as no effect of DPH concentration on the cmc was observed (for DPH concentration range 0.0025–0.025 mM) by Chattopadhyay and London.[32]

Effect of Methanol. The aqueous block copolymer solutions used for the determination of the cmc and cmt contained approximately 1% methanol; methanol was used to dissolve DPH, the latter being sparingly soluble in water. Methanol was also used in the preparation of a solution of high-concentration polycyclic aromatic hydrocarbons (PAHs), employed in PAH solubilization experiments from aqueous solutions by Edwards et al.[34] They found that methanol was a preferred solvent, as their tests showed no effect on surfactant solubilization; most higher alcohols could not be utilized since they affected the cmc values significantly.[42] Measured apparent PAH solubilities at zero surfactant concentration in the presence of 1% by volume methanol appear to be enhanced by $\sim$20–30% relative to reported solubilities in pure water. The presence of methanol did not shift the cmc or the slope of the solubilization curve for a solution of pyrene and octylphenol PEO surfactant.[34] Bedo et al.[43] studied the effect of methanol, ethanol, and isopropyl alcohol on the micellization of ethoxylated nonylphenols, and their data suggest that 1% methanol increased the cmc by approximately 40%; isopropyl alcohol had a far more pronounced effect on the cmc. The sample preparation for the cmc determination of Chattopadhyay and London[32] involved dissolving PDH in THF and adding 1 μL to 2 mL of surfactant solution. These authors found that up to 1–2% (v/v) THF had little effect on the cmc for several detergents.

Spectroscopy. Emission fluorescence spectra of the copolymer/DPH/water samples were obtained with a Shimadzu RF-5000 recording spectrofluorophotometer, using an excitation wavelength of 350 nm and emission wavelength range 350–650 nm. The emission intensity peak used to observe the DPH solubilization in the copolymer micelles was at 457 nm. UV-vis absorption spectra of the copolymer/DPH/water samples were recorded in the 300–500-nm range using a Perkin-Elmer Lambda 3B UV/vis spectrophotometer, controlled by the Perkin-Elmer Computerized Spectroscopy Software (PECSS). The main absorption intensity peak, characteristic of DPH, was at 356 nm. For both fluorescence and absorption spectroscopy experiments, the samples were placed in Teflon-stoppered quartz cuvettes. Temperature control within 0.05 °C was achieved using a Neslab RTE-110 refrigerated bath/circulator. The temperature range employed was 15–55 °C, as measured in the thermostated photometer reference cell. At least 1 h was allowed for the sample temperature equilibration. After establishing that emission fluorescence spectroscopy gave the same results as visible absorption spectroscopy, we used the latter to obtain the data reported here (the absorption spectrum of a molecule is, in principle, the same as the fluorescence excitation spectrum, which, in turn, is the mirror image of the fluorescence emission spectrum[44]).

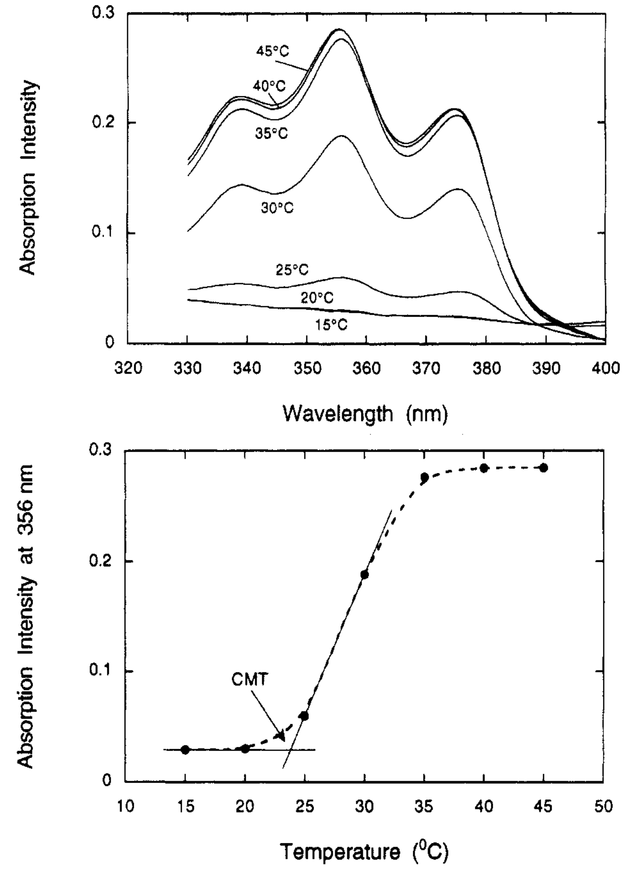

Figure 1. Effect of temperature on (a, top) UV-vis absorption spectra and (b, bottom) the absorption intensity at 356 nm for DPH in a 0.5% w/v solution of Pluronic P104. The estimation of the critical micellization temperature from the data is indicated in b.

Results and Discussion

UV-vis spectra of aqueous Pluronic solutions with concentrations from 0.001 to 20% w/v containing DPH were taken at 5 °C temperature intervals over the range 15–55 °C. At low concentrations and/or low temperatures, the Pluronics did not associate in aqueous solution, DPH was not solubilized in a hydrophobic environment, and, as a result, the fluorescence and UV-vis intensities due to DPH were very low. At higher concentrations and/or temperatures, the Pluronics formed micelles, and DPH was solubilized in the hydrophobic micelle interior, giving a characteristic spectrum. Figure 1a shows the UV-vis absorption spectra of a typical DPH/Pluronic/water solution (P104, 0.5% w/v) at different temperatures and Figure 1b the absorption intensity at 356 nm of the previous sample, as a function of temperature. The cmt values for

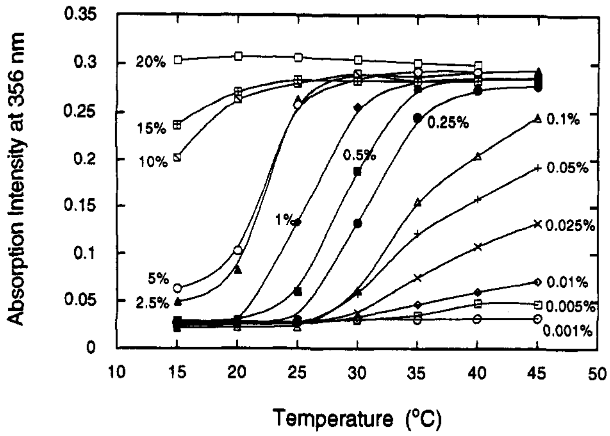

Figure 2. Temperature effects on the absorption intensity of DPH at 356 nm in aqueous solutions of Pluronic P104 of various concentrations. The critical micellization temperatures can be estimated from the first break in the curves.

Pluronics of various concentrations were obtained from the first inflection of the absorption intensity at 356 nm vs temperature plot.

Critical Micellization Temperature Data. Figure 2 shows the dependence of the intensities at 356 nm (spectral maximum due to DPH) on temperature, for various concentrations of a typical Pluronic (P104) aqueous solution. The critical micellization temperature values were obtained from the first inflection of the intensity vs temperature sigmoidal curve (or alternatively from the first appearance of a well-defined peak in the sample spectrum) that indicated the formation of a hydrophobic domain. This domain appears to be the result of aggregation of many Pluronic molecules to form a micelle, rather than the coiling of a single molecule. Dye solubilization experiments with random PEO/PPO copolymers of similar PEO/PPO composition and block PPO–PEO–PPO copolymers of comparable PEO and PPO segment sizes showed no increase in the absorption intensity due to the DPH, indicating that the existence of hydrophobic (PPO) patches in a single molecule are not sufficient for solubilization of DPH. The second inflection of the intensity vs temperature sigmoidal curve was indicative of the complete solubilization of DPH in the block copolymer micelles. The use of DPH solubilization to determine cmt proved to be a reliable and reproducible method; the uncertainty in the cmt values reported here is less than ±1 °C (the uncertainties in the cmt values arose mainly from the use of lines tangent to parts of the intensity vs temperature curve for deriving the temperature corresponding to the cmt). There was some difficulty involved in the cmt determination only for L64, as the samples became turbid in the vicinity of micelle formation.[10]

The cmt values obtained for various Pluronics are listed in Table 2 as a function of copolymer concentration, expressed in both percent w/v and mM concentration units. To the best of our knowledge, this is the first comprehensive compilation of cmt data for aqueous Pluronic solutions and the only one available for F123, P103, P104, P105, F108, P84, and P65; such a data set should prove to be useful for the numerous applications of Pluronics that depend on their micelle forming abilities. The few cmt values available in the literature agree well with our data: 15 °C cmt for 10% F127 solution reported in ref 45, compared to our 16 °C; 25 °C cmt for 5% P85 solution reported in ref 13 compared to our 25 °C; 25 °C cmt for 6% L64 solution reported in ref 46 compared to our 26 °C. Furthermore, the cmt values obtained from the DPH solubilization method compare very well to the onset of pyrene and naphthalene solubilization in L64, P104, and F108.[47] The agreement between our cmt data (from dye solubilization experiments) and cmt data from light scattering intensity is not as good for F68; Zhou and Chu[10] obtained cmt values of 42.3, 39.0, and 36.3 °C for 1.25, 2.50, and 5.17% polymer concentrations, respectively, compared to our 46 and 40 °C for 2.5 and 5.0%, respectively. F68 is fairly hydrophilic (80% PEO) and may form premicellar aggregates discernible with light scattering but with no well-defined hydrophobic core to allow for DPH solubilization.

Critical Micellization Concentration Data. Figure 3 shows the dependence of the intensities at 356 nm (spectral maximum due to DPH) on Pluronic P104 concentration, at various temperatures. The critical micellization concentration was estimated again from the first inflection of the intensity vs log concentration sigmoidal curve; the uncertainty in the cmc values reported is less than ±15% (the uncertainties in the cmc values arose similarly to those discussed for cmt). Table 3 lists the cmc values for various Pluronics as a function of solution temperature.

Given the number of publications dealing with aqueous solutions of Pluronics, there are surprisingly few reliable cmc data for Pluronics. The cmc values we obtained are generally 1 order of magnitude higher than the values reported by Schmolka and Raymond[35] for F68, P84, P85, F88, P104, and F108. Prasad et al.[48] measured the surface tension of aqueous Pluronic solutions (L64, F68, P85, and F88) and detected in several systems two points of inflection in the surface tension vs log concentration plots. They interpreted this as due to the formation of so-called "monomolecular" aggregates in dilute solution and multimolecular aggregates in more concentrated solutions. Wanka et al.[11] found that the surface tension of P104, P123, and F127 decreased linearly with the logarithm of the copolymer concentration according to the Gibbs isotherm of adsorption over several concentration decades. At a characteristic concentration, there was a break in the curve; the surface tension kept decreasing with further increase in concentration, but with a smaller slope, until a second concentration was reached above which the surface tension remained constant. This transition region extended approximately 1 concentration decade. According to Wanka et al., the two breaks in the curves could be interpreted as being due to the existence of two critical concentrations; taking other types of measurements into account, however, it seemed more conceivable that the transition region could be related to the fact that the block copolymers were not well-defined samples but had a broad molecular weight distribution.[11] In addition, any trace impurities (originating from the manufacturing process) in the polymer solutions would have a significant effect on surface tension measurements. Interestingly enough, the concentrations at the second inflection point from ref 11 (0.3% for F127 and 0.01% for P104, both at 25 °C) and ref 48 are comparable to the cmc values found in our study. Two breaks can also be observed in a surface tension data set for P94 published by Bahadur and Pandya,[49] who derived the cmc from the first break. In detailed surface tension measurements with the same copolymers used for the dye solubilization experiments (to avoid inconsistency due to different polymer batches), we have also observed the two inflection points in the surface tension curves.[50]

The ambiguities in the different ways of measuring the cmc in Pluronic solutions point to the need to define clearly the applications for which the data are intended. The dye solubilization method for determining the cmc is ideal for

Table 2. Critical Micellization Temperatures for Pluronic Copolymer Aqueous Solutions as a Function of Copolymer Concentration

	L64		P65		F68		P84		P85		F88	
concn, % w/v	mM	CMT	mM	CMT	mM	CMT	mM	CMT	mM	CMT	mM	CMT
0.01		–		–		–	0.024	46.5	0.022	46.5		–
0.025	0.086	44.5		–		–	0.059	42.5	0.054	43		–
0.05	0.172	42	0.147	49		–	0.119	39.5	0.109	40	0.044	52.5
0.1	0.345	39.5	0.294	46		–	0.238	37	0.217	37.5	0.088	48.5
0.25	0.862	36.5	0.735	42		–	0.595	33.5	0.543	33.7	0.219	45
0.5	1.72	34	1.47	39	0.595	52.5	1.19	31	1.09	32	0.439	41
1.0	3.45	31.5	2.94	36	1.19	50	2.38	28.5	2.17	29.5	0.877	38
2.5	8.62	28.5	7.35	31.5	2.98	46	5.95	25.5	5.43	27	2.19	34
5.0	17.2	26.5	14.7	28.5	5.95	40	11.9	23	10.9	25	4.39	30.5
10	34.5	23.5	29.4	25.5	11.9	33	23.8	19		–	8.77	26
15		–		–	17.9	27		–		–	13.2	21.5

	P103		P104		P105		F108		P123		F127	
concn, % w/v	mM	CMT	mM	CMT	mM	CMT	mM	CMT	mM	CMT	mM	CMT
0.01	0.02	29.5	0.017	33.5	0.015	32		–	0.017	26		–
0.025	0.05	27.5	0.042	31	0.038	30	0.017	40.5	0.043	24	0.02	35.5
0.05	0.101	26	0.085	29.5	0.077	28.5	0.034	38	0.087	22.5	0.04	33
0.1	0.202	24.5	0.169	27.5	0.154	27	0.068	36	0.174	21	0.079	31
0.25	0.505	22.5	0.424	25.5	0.385	25	0.171	33.5	0.435	19	0.198	28
0.5	1.01	21	0.847	23.5	0.769	23.5	0.342	31.5	0.87	17.5	0.397	26.5
1.0	2.02	19.5	1.69	21.5	1.54	21.7	0.685	29.5	1.74	16	0.794	24
2.5		–	4.24	19.5	3.85	19.5	1.71	27	4.35	14	1.98	21.5
5.0		–	8.47	18		–	3.42	24.5	8.70	12.5	3.97	19.5
10		–		–		–	6.85	21		–		–
15		–		–		–		–		–		–

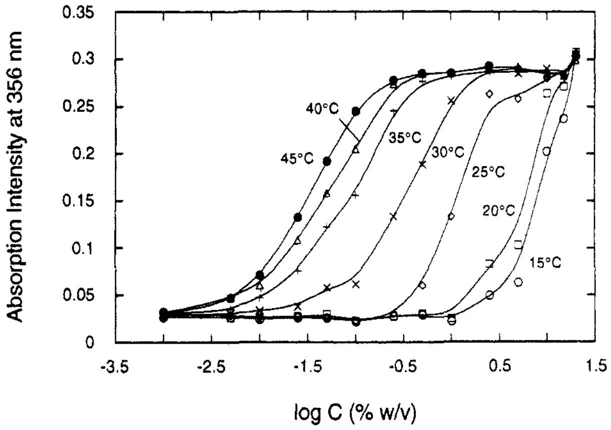

Figure 3. Effect of concentration, with temperature as parameter, on the absorption intensity of DPH at 356 nm in aqueous solutions of Pluronic P104. The critical micellization concentrations can be estimated from the first break in the curves.

determining the range of solubilization enhancement of otherwise sparingly soluble organics in the presence of Pluronic copolymers, provided the molecules to be solubilized are of comparable hydrophobicity and size to DPH. In fact, the partition coefficient for DPH in the copolymer micelles can be estimated from the same set of data used to obtain the cmc values. The molar solubilization ratio (MSR), defined as the number of moles of organic compound solubilized per mole of surfactant added to solution, is a measure of the effectiveness of a particular surfactant in solubilizing a given solubilizate.[26] The increase in solubilizate concentration per unit increase in micellar surfactant concentration is equivalent to the MSR. In the presence of excess hydrophobic organic compound, the MSR may be obtained from the slope of the curve that results when the solubilizate concentration is plotted against surfactant concentration.[34] The effect of copolymer PPO/PEO composition, molecular weight, solution concentration and temperature on the molar solubilization ratio of DPH in aqueous block copolymer solutions will be presented in detail elsewhere.[50]

cmc and cmt Values as a Function of Pluronic Structure and Molecular Weight. The cmc and cmt values listed in Tables 2 and 3 are discussed in this section in terms of the number of propylene oxide (PO) and ethylene oxide (EO) units in the Pluronic block copolymer molecules. This enables estimation of the effect of the polymer structure and molecular weight on micellization behavior.

PPO Effect. The cmc values for Pluronics P65, P84, and P123, which have the same hydrophilic (PEO) segment and varying hydrophobic (PPO) segment, are plotted semilogarithmically in Figure 4a as a function of the number of PO units in the Pluronic molecule, for different solution temperatures (25, 35, and 45 °C). The log(cmc) values for the Pluronics solutions (at a given solution temperature) decreased in a roughly linear fashion ($R^2 > 0.99$) as a function of PO units, indicating that polymers with a larger hydrophobic (PO) domain form micelles at lower concentrations. Higher temperatures resulted in lower cmc values, with the slope of the log(cmc) vs PO number curve increasing with temperature. The cmt values for the Pluronics solutions (at a given copolymer concentration) decreased as a function of PO units, as shown in Figure 4b, indicating that polymers with a larger hydrophobic domain form micelles at lower temperatures.

PEO Effect. The cmc and cmt values for groups of Pluronics with the same hydrophobic segment and varying hydrophilic segment, e.g., with 30 (L64, P65, F68), 40 (P84, P85, F88), and 60 (P104, P104, F108) PO units, plotted as a function of EO units (plot not shown), show a small increase in the cmc and cmt with increasing number of EO units. This would indicate that the micelle formation becomes more difficult the more hydrophilic the molecules, although the effect of PEO on the cmc and cmt is less pronounced than that of PPO, intimating that PPO is a primary factor in the micellization process.

Molecular Weight Effect. The cmc and cmt values for copolymers of constant PPO/PEO ratio but varying molecular weight decrease with increasing number of EO units (at a given copolymer solution temperature and concentration for the cmc and cmt, respectively). It can

Table 3. Critical Micellization Concentrations for Pluronic Copolymer Aqueous Solutions as a Function of Solution Temperature

	L64		P65		F68		P84		P85		F88	
temp, °C	% w/v	mM	% w/v	mM	% w/v	mM	% w/v	mM	% w/v	mM	% w/v	mM
20	–		–		–		–		–		–	
25	–		–		–		2.6	6.190	4	8.695	–	
30	1.5	5.172	4	11.76	–		0.6	1.428	0.9	1.956	–	
35	0.4	1.379	1	2.941	–		0.15	0.357	0.2	0.434	1.7	1.491
40	0.1	0.344	0.35	1.029	7	8.333	0.04	0.095	0.05	0.108	0.6	0.526
45	0.02	0.069	0.1	0.294	3	3.571	0.013	0.031	0.014	0.030	0.24	0.210
50	–		0.04	0.117	0.9	1.071	–		–		0.09	0.079
55	–		–		0.3	0.357	–		–		0.04	0.035

	P103		P104		P105		F108		P123		F127	
temp, °C	% w/v	mM	% w/v	mM	% w/v	mM	% w/v	mM	% w/v	mM	% w/v	mM
20	0.7	1.414	2	3.389	2.2	3.384	–		0.18	0.313	4	3.174
25	0.07	0.141	0.3	0.508	0.3	0.461	4.5	3.082	0.03	0.052	0.7	0.555
30	0.01	0.020	0.04	0.067	0.025	0.038	0.8	0.547	0.005	0.009	0.1	0.079
35	0.002	0.004	0.008	0.013	0.005	0.007	0.15	0.103	0.001	0.002	0.025	0.019
40	–		0.002	0.003	0.001	0.001	0.04	0.027	–		0.008	0.006
45	–		–		–		0.008	0.005	–		–	
50	–		–		–		–		–		–	
55	–		–		–		–		–		–	

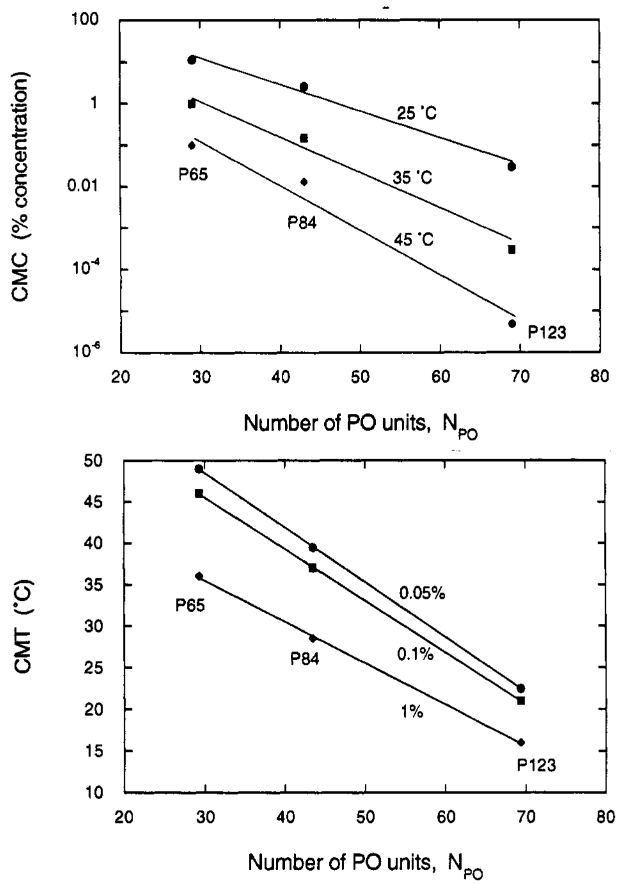

Figure 4. (a, top) Critical micellization concentrations and (b, bottom) critical micellization temperatures of Pluronic copolymers, having the same number of EO units, as a function of the number of PO units.

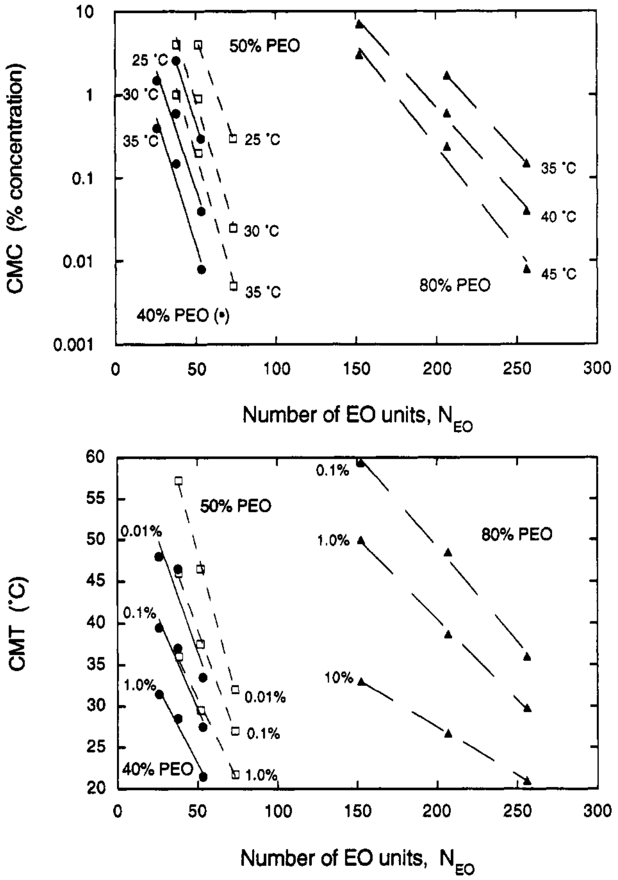

Figure 5. (a, top) Critical micellization concentrations for Pluronic copolymers at various solution temperatures and (b, bottom) critical micellization temperatures at various copolymer concentrations, as a function of the number of EO units, for copolymers of 40, 50, and 80% EO content.

thus be concluded that, for given PPO/PEO ratio, Pluronics of higher molecular weight form micelles more readily, e.g., at lower concentrations and temperatures. Parts a and b of Figure 5 show the cmc and cmt values, respectively, for various Pluronics as a function of the number of EO units, for groups of copolymers with 40% (L64, P84, P104), 50% (P65, P85, P105), and 80% (F68, F88, F108) PEO content and at various copolymer solution temperatures (in Figure 5a) and concentrations (in Figure 5b). The cmt values were influenced more by molecular weight the lower the relative EO content and the lower the copolymer concentration, as is evidenced by the steeper slopes for the curves for these conditions. A linear fit was found to describe adequately the cmc and cmt dependence on the number of EO units for copolymers of constant relative PEO content and varying molecular weight ($R^2 >$ 0.98 for Figure 5a, while $R^2 > 0.94$ for 40% PEO and R^2 > 0.99 for 50 and 80% PEO in Figure 5b).

Comparison of Pluronic cmc and cmt Values to Those of C_iE_j Nonionic Surfactants. It is interesting to compare the micellization of Pluronic block copolymers to that of C_iE_j (j ethylene glycol–i alkyl ethers) low molecular weight nonionic surfactants, which has been more widely studied.[51,52] In the latter systems, it was found that the cmc decreased and that the micellar size increased strongly, both with increasing temperature. Thus, in these respects, the analogy between Pluronics and C_iE_j seems valid. However, the pronounced sensitivity of the cmc to temperature, or of the cmt to concentration, as found here for many Pluronics, is not evident with the *n*-alkyl poly(ethylene glycol) ethers, C_iE_j.[53] The decrease of the hydrophilicity of the PEO blocks with increasing temperature has comparatively little effect on the cmc for C_iE_j: for $C_{12}E_8$ the cmc is reported as 9.7×10^{-5} M at 15 °C and 5.8×10^{-5} M at 40 °C (~40% decrease in the cmc for 25 °C increase in temperature).[53] In the case of Pluronic copolymer solutions, a 10 °C decrease in temperature results in changes of the cmc by more than an order of magnitude (see Figure 5a). Also, the number of EO units has little effect, at least for short EO headgroups: the cmc is given as 6.5×10^{-5} M for $C_{12}E_5$ and 7.2×10^{-5} M for $C_{12}E_8$.[53] For longer EO chains ($C_{16}E_j$, j = 17, 32, 44, 63), log(cmc) increased linearly as a function of EO weight fraction, the cmc varying by up to an order of magnitude over the EO range studied, the slope being steeper at higher temperatures.[51] Although the increase in the cmc with increasing EO may appear significant for the $C_{16}E_j$, j = 17, 32, 44, 63, surfactant series, the change in the cmc per EO unit in this case is less pronounced than the cmc change between $C_{12}E_5$ and $C_{12}E_8$. In the case of Pluronics, the change in cmc per EO unit was found to be even smaller, indicating that the influence of PEO on cmc diminishes as the size of the surfactant increases. This can be observed in Figure 5a where, for the same change of cmc, it takes 50 EO units for Pluronics of high molecular weight (80% EO group) but only 10 EO units for the lower molecular weight Pluronics. The main determinant of the cmc for C_iE_j was found to be the length of the alkyl (hydrophobic) chain. The logarithm of cmc for the C_iE_8, i = 10–15, series decreased linearly with increasing carbon number in the alkyl chain (cmc varied by approximately 2.5 orders of magnitude over the carbon number range studied).[52] For the Pluronics, an increasing hydrophobicity of the PO block with increasing temperature, in combination with the size polydispersity of the PO blocks, has been advanced as the reason for the strong temperature dependence of the cmc.[54]

Thermodynamics of Block Copolymer Micelle Formation. It is well established that block copolymers of the A–B or A–B–A type form micelles in selective solvents which are thermodynamically good solvents for one block and precipitants for the other block. In general, micellization of block copolymers, as in the case of conventional detergents, obeys the closed association model, which assumes an equilibrium between molecularly dispersed copolymer (unimer) and multimolecular aggregates (micelles).[24,55] There are two main approaches to the thermodynamic analysis of the micellization process: the phase separation model, in which the micelles are considered to form a separate phase at the cmc, and the mass-action model that considers micelles and unassociated monomers in association–dissociation equilibrium.[26] In both approaches, the standard free-energy change for the transfer of 1 mol of amphiphile from solution to the micellar phase (free energy of micellization), $\Delta G°$, in the absence of electrostatic interactions (nonionic surfactants) is given by[26,27]

$$\Delta G° = RT\ln(X_{\mathrm{cmc}}) \tag{1}$$

where R is the gas law constant, T is the absolute temperature, and X_{cmc} is the critical micellization concentration in mole fraction units. It is assumed here that the concentration of free surfactant in the presence of micelles is constant and equal to the cmc value, in the case of the phase separation model, or that the micelle aggregation number is large for the mass-action model. Applying the Gibbs–Helmholtz equation and assuming the aggregation number to be independent of temperature in the case of the mass-action model, we can express the standard enthalpy of micellization, $\Delta H°$, as[26,27]

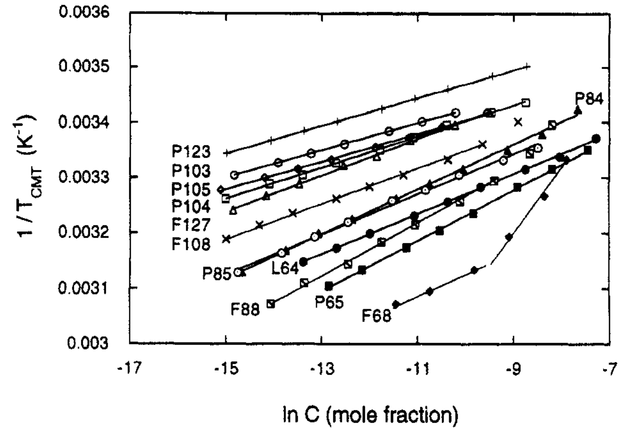

Figure 6. Reciprocal T_{cmt} vs copolymer concentration plots for various Pluronics, used for the determination of the micellization enthalpy in terms of the closed association model.

$$\Delta H° = -RT^2[\partial\ln(X_{\mathrm{cmc}})/\partial T]_P = R[\partial\ln(X_{\mathrm{cmc}})/\partial(1/T)]_P \tag{2}$$

Finally, the standard entropy of micellization per mole of surfactant, $\Delta S°$, can be obtained from

$$\Delta S° = (\Delta H° - \Delta G°)/T \tag{3}$$

It has been shown for block copolymer micellization[17,56,57] that, within experimental error,

$$\partial\ln(X_{\mathrm{cmc}})/\partial(1/T) = \partial\ln(X)/\partial(1/T_{\mathrm{cmt}}) \tag{4}$$

where X is the concentration expressed as mole fraction and T_{cmt} is the critical micellization temperature; thus, eq 2 becomes

$$\Delta H° = R[\partial\ln(X)/\partial(1/T_{\mathrm{cmt}})]_P \tag{5}$$

$1/T_{\mathrm{cmt}}$ vs ln(X) Plot: Mode of Copolymer Association. In accordance with eq 5, the inverse cmt values were plotted as a function of the logarithm of copolymer concentration (mole-fraction units) for a number of Pluronics, as shown in Figure 6. We chose to use this representation (cmt for a given concentration) instead of eq 2 (cmc for a given temperature) as it more closely reflects our experimental procedures, where the temperature of a sample of given polymer concentration was varied. The cmt data, plotted in this manner, are generally described well by a straight line. Exceptions to the linear fit are F68, F88, and F108, for which the slopes appear to increase at high concentrations (>5% w/v). These three polymers are all hydrophilic and of high molecular weight; it may be that for them the simple assumptions of the thermodynamic analysis do not hold well at high polymer concentrations. The hydrated PEO chains of the micelle coronas will overlap and entangle with increasing polymer concentration, up to the formation of a gel-like structure (F108 of 20% w/v forms a gel at room temperature).

One of the assumptions involved in deriving eqs 1–5 is that the micelle aggregation number is independent of

Table 4. Standard Free Energies ($\Delta G°$), Enthalpies ($\Delta H°$), and Entropies ($\Delta S°$) of Micellization of Various Pluronic Copolymers at Their Critical Micellization Temperature for 1% Solutions

polymer	MW	PPO/PEO	$\Delta H°$, kJ/mol	$\Delta G°$, kJ/mol	$\Delta S°$, kJ/(mol K)
L64	2 900	1.155	230	-24.5	0.835
P65	3 400	0.766	182	-25.3	0.671
F68	8 400	0.190	215	-28.8	0.756
P84	4 200	1.149	211	-25.2	0.784
P85	4 600	0.764	229	-25.5	0.842
F88	11 400	0.190	169	-28.5	0.638
P103	4 950	1.791	339	-24.8	1.244
P104	5 900	1.146	296	-25.4	1.092
P105	6 500	0.763	331	-25.6	1.212
F108	14 600	0.190	266	-28.4	0.975
P123	5 750	1.788	329	-24.9	1.223
F127	12 600	0.326	253	-27.5	0.944

temperature. Although there are some studies (e.g., ref 10 for F68, ref 15 for P85, ref 54 for L64, and ref 58 for F127) indicating an increase in the aggregation number with temperature, eq 5, based on a closed association model, correlated the cmt data in a satisfactory way. Consequently, we did not attempt to fit a stepwise association model to our data set, as that would have required an additional degree of freedom with no enhancement in the fit of the data. Reddy et al.[12] examined the mode of association of a purified L64 sample in aqueous solutions by measuring the light scattering intensity as a function of temperature and concentration. The association at 34.5 and 40 °C was described by a cooperative association model which assumed aggregate growth by stepwise addition of unimers. Deviation of the experimental curves from the computed curves was observed at high concentrations and attributed to solution nonideality.[12] It should be noted, though, that the data set used for the analysis of ref 12 was relatively limited. A concentration-independent diffusion coefficient and micelle weight-average molecular weight have been explained by a closed association model for hexa(oxyethylene glycol) monoether micelles.[59] The use of a closed association model in the case of the copolymer we studied appears well justified based on the good fit of the data to eq 5; we consequently employed such as model for estimating $\Delta H°$ and $\Delta S°$ of the micellization process.

$\Delta G°$ $\Delta H°$, and $\Delta S°$ as a Function of Pluronic Structure and Molecular Weight. The standard enthalpy of micellization, $\Delta H°$, was calculated from the inverse slope of the linear fit to the $1/T_{\mathrm{cmt}}$ vs ln(mole fraction) data, in accordance with eq 5. $\Delta H°$ values, together with $\Delta G°$ and $\Delta S°$ (calculated from eq 1 and 3, respectively, at the critical micellization temperature for 1% copolymer solutions), are listed in Table 4 for various Pluronics. It is emphasized that these data are for a *constant cmc, and not constant temperature* (for any given concentration, there is a unique cmt; conversely, for any given temperature, there is a unique cmc). The values for the tabulated $\Delta H°$, $\Delta G°$, and $\Delta S°$ range between 169 and 339 kJ/mol, -24.5 and -28.8 kJ/mol, and 0.638 and 1.244 kJ/(mol K), respectively. The higher values of $\Delta H°$, $\Delta G°$, and $\Delta S°$ were observed for P103 and L64 (relatively hydrophobic copolymers), while the lower values were observed for the relatively hydrophilic copolymers F68 and F88.

The standard enthalpy of micellization, $\Delta H°$, is positive, indicating that the transfer of unimers from solution to the micelle is an enthalpically unfavorable endothermic process. The free energy, $\Delta G°$, is negative, since thermodynamically stable micelles are formed spontaneously. Thus, it is clear that a negative entropy contribution must be the driving force for micellization of the block copolymers. The tradiational view of micelle formation[60] has been based on the study of the solubility of hydrocarbons in water and what has come to be known as the hydrophobic effect.[61] The presence of hydrocarbon molecules in water causes a significant decrease in the water entropy, suggesting that it induces an increase in the degree of structuring of the water molecules, owing to cavity formation. When hydrocarbon residues aggregate in aqueous solution to form a micelle, the hydrogen-bonding structure in the water is, to a large extent, restored and the water entropy increases; this overcomes the loss of entropy due to the localization of the hydrocarbon chains in the micelles. The entropy contribution usually dominates the micellization process in aqueous surfactant solutions, with the enthalpy playing a minor role. In the Pluronic copolymers, the unfavorable enthalpy component is significant but is, nevertheless, overcome by an even stronger entropy effect. In contrast to the entropy-driven micellization in water, the micellization of copolymers in nonpolar solvents originates from enthalpy interactions between the copolymer segments and the solvent.[24]

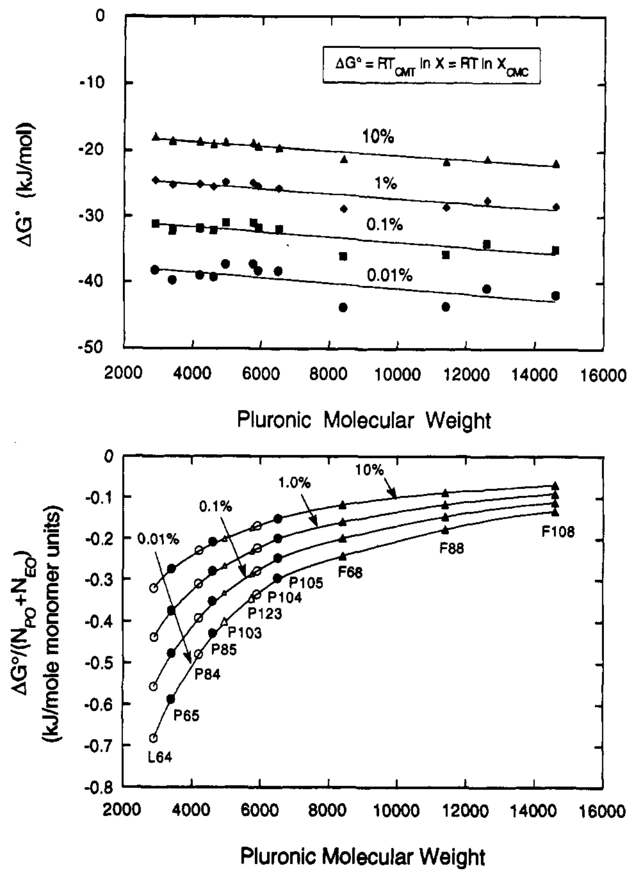

Figure 7. Effect of Pluronic molecular weight on the free energies of micellization for various polymer concentrations expressed as (a, top) $\Delta G°$ (kJ/mol) and (b, bottom) $\Delta G°/(N_{\mathrm{EO}} + N_{\mathrm{PO}})$ (kJ/mol of monomer unit).

Free energies of micellization per mole of polymer in solution, $\Delta G°$, calculated at the critical micellization temperatures for the various copolymers at different solution concentrations are shown as a function of Pluronic molecular weight in Figure 7a. Although the data exhibit some scatter, presumably because of the widely varying composition ratios of the polymers used in this study, they do indicate the tendency for higher molecular weight copolymers to have more negative free energies of micellization, indicating a greater propensity to form micelles with increasing polymer chain length. This is despite the fact that the larger polymers are generally more hydrophilic, as they are composed predominantly of ethylene oxide groups.

The data shown in Figure 7a collapse into a single smooth curve, independent of copolymer composition ratio PPO/PEO, when normalized with respect to the total number of monomer units in the polymer, $N_{EO} + N_{PO}$, as shown in Figure 7b. It can be seen clearly that the lower molecular weight, more hydrophobic Pluronics correspond to more negative ΔG° per monomer unit values. These data were correlated as a function of molecular weight M_W and concentration, C, by the empirical equation

$$\Delta G^\circ/(N_{EO} + N_{PO}) = A_1 \tan^{-1}(M_W) + A_2 \qquad (6)$$

where A_1 and A_2 are concentration-dependent constants given by

$$A_1 = 1263\text{–}360.5 \log(C) \qquad (7)$$

and

$$A_2 = -1985 + 566.3 \log(C) \qquad (8)$$

respectively. The fit is good ($R^2 > 0.997$), and the predictions of the correlation for $\Delta G^\circ/(N_{EO} + N_{PO})$ (kJ/monomer unit) differ at most by 2.5% from the experimentally determined values. Since this correlation holds for PEO-PPO-PEO copolymers covering a wide range of molecular weights and PPO/PEO compositions, it can be used for predicting ΔG° for copolymers that have not yet been studied experimentally. Once ΔG° is known, the critical micellization concentrations and temperatures can also be estimated.

The normalization of the data in this fashion enables the composition ratio effects to be decoupled from the effects of overall molecular weight and copolymer concentration on the micellization process. The reason for the success of this normalization is unclear. It may reflect the importance of the ether oxygens, common to both monomer types in the polymer, in determining the polymer–polymer and polymer–solvent interactions. These interactions can have both enthalpic and entropic contributions, as is discussed later. The unfavorable entropic effects associated with the localization of the polymers within the micelles would then be reflected in the molecular weight dependency, as the absolute value of the free energy per monomer becomes smaller with increasing polymer molecular weight. It must be emphasized again, however, that the curves presented here are at constant concentration and that the temperature, which is the cmt, is different for each polymer datum point.

To further probe the origin of micelle formation in Pluronic copolymer solutions, the dependence of the thermodynamic parameters ΔH° and ΔG° on the PPO/PEO composition ratio was examined. Figure 8a shows that the normalized ΔH° (expressed in kJ/mol of average monomer unit) approaches zero as the PPO/PEO ratio goes to zero. It can thus be inferred that the micellization process is dominated by the PPO (hydrophobic) part of the copolymer. A similar trend was observed by Armstrong et al.[62] based on DSC enthalpy changes of ICI Poloxamer solutions and by Williams et al.[63] using the increment in apparent molar volume on "thermal transition" of PolyScience PEO-PPO copolymers as a function of PPO/PEO. The fact that the normalized ΔH° values are approximately the same for different Pluronics of a constant PPO/PEO ratio would indicate that the micellization enthalpy per monomer unit is independent of molecular weight. In contrast to the trend of decreasing ΔG° with increasing Pluronic molecular weight, there is no definite dependence of ΔH° on molecular weight over the range covered in this study. The ΔH° data presented in Table 4 reveal two main groups of copolymers, the relatively hydrophobic P103, P104, P105, and P123 with ΔH° in the 300–350 kJ/mol range and the relatively hydrophilic L64, P65, P84, and P85 with ΔH° in the 180–230 kJ/mol range, while ΔH° for the other four copolymers ranges from 170 to 270 kJ/mol. The dependence of the normalized ΔH° on the copolymer composition is far more instructive and is presented in Figure 8a. A plot of ΔG° of micellization (expressed in kJ/mol of average monomer unit) as a function of PPO/PEO (Figure 8b) again shows the ΔG°/unit values approaching zero as the PPO/PEO ratio goes to zero. The unit free energy, however, decreases (becomes more negative) with a decrease in molecular weight for Pluronics with a constant PPO/PEO ratio.

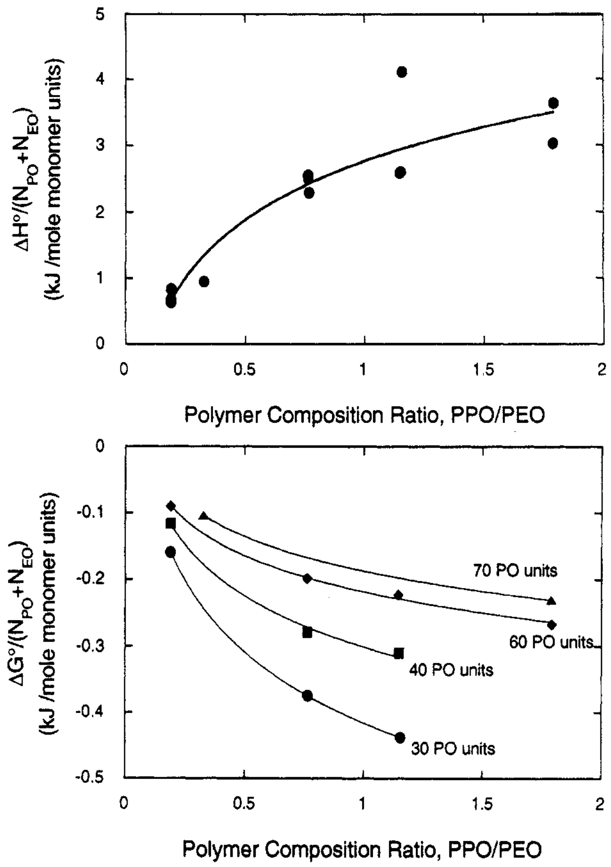

Figure 8. Effect of polymer composition ratio, PPO/PEO, on (a, top) $\Delta H^\circ/(N_{EO} + N_{PO})$ and (b, bottom) $\Delta G^\circ/(N_{EO} + N_{PO})$.

The compilation of ΔG°, ΔH°, and ΔS° data for a wide range of Pluronic block copolymers presented in this paper is, to the best of our knowledge, the most complete in the literature. In a previous investigation, Reddy et al.[12] estimated the ΔG° of micellization at −20 kJ/mol and the ΔH° of micellization at 200 kJ/mol for a solution of purified L64, utilizing ln(cmc) vs $1/T$ data (only three data points, though). The same group[17] reported the ΔH° of micellization at −316 ± 20 kJ/mol for a solution of purified F127 (from ln(concentration) vs $1/T_{cmt}$ data). These values are close to our estimates of $\Delta G^\circ = -24.5$ kJ/mol and $\Delta H^\circ = 230$ kJ/mol for L64 and $\Delta H^\circ = 253$ for F127 (the copolymers we used were not purified).

ΔH° from Differential Scanning Calorimetry. Another method for obtaining estimates of the free enthalpy of micellization, ΔH°, is differential scanning calorimetry (DSC). DSC measurements for aqueous Pluronic solutions show broad endothermic peaks, typical for a first-order phase transition, at concentration-dependent characteristic temperatures.[11,62] The peaks have rather high enthalpy values (almost 3 orders of magnitude larger than typical enthalpy values for phase transitions in lyotropic liquid crystals[11] and are rather broad, extending more than 20 °C. The latter can be due to the fact that the copolymers are not pure compounds but show a broad molecular weight distribution; it is well-known also that melting peaks become broad in the presence of impurities.[11] It should be pointed out here that the enthalpy change measured by the peak area in DSC is not the standard enthalpy change but depends upon the real states of the chains before and after micellization. The standard state enthalpy change is defined for transfer of 1 mol of chains from the ideally dilute solution to the solvated micellar state. In the ideally dilute solution, copolymer segments interact only with solvent, whereas in real solutions segments also interact with each other, and this may cause discrepancies between micellization enthalpies obtained from DSC and the ones derived from an analysis similar to ours.[64] It has also been reported by Hiemenz[65] that $\Delta H°$ values calculated by a micellization thermodynamics model generally show poor agreement with those determined calorimetrically, at least for ionic surfactants.

From a very limited set of data (P123, F127, and P104 studied with DSC), Wanka et al.[11] observed no proportionality between the enthalpy values and the size of the EO portion of the molecules, but they noted that there was proportionality between these values and the PO groups, to a first approximation. From this they concluded that the transition is probably due to the dehydration or "melting" of the PO groups.[11] Similar trends were observed in our $\Delta H°$ data. It appears, though, from our data set that there is a weak effect of EO on $\Delta H°$. For Pluronics with the same size hydrophobic (PPO) segment and varying size hydrophilic (PEO) segment, i.e., P103, P104, P105, and F108, $\Delta H°$ decreased by $\sim$15% as the number of EO segments increased from 2×17 to 2×132. On the contrary, for Pluronics with the same size hydrophilic (PEO) segment and varying size hydrophobic (PPO) segment, i.e., P65, P84, and P123, $\Delta H°$ increased by $\sim$100% as the number of PO segments increased from 30 to 70. The PPO effect was more significant and, together with the data of Figure 8, leads to the conclusion that PPO is mainly responsible for the micellization of Pluronics.

Differential scanning calorimetry was also used by Beezer et al.[66] on PEO-PPO-PEO block copolymer solutions. The observed "phase transitions" were in the 100–300 kJ/mol range and were initially thought to result from changes in the polymer solvation as the temperature changed. The authors claimed[66] that, at the concentration used (5 g/L), only monomeric species were present in solution. In a more recent paper from the same group, Armstrong et al.[62] concluded that the observed enthalpy change is indicative of an aggregation process, accompanied by desolvation and change in conformation of the hydrophobe. Although direct comparison between the calorimetry ΔH values of refs 62 and 66 and our $\Delta H°$ cannot be made as the copolymers used were not the same, our data strongly suggest that the micellization process is the major contribution to the calorimetrically observed enthalpy change.

Molecular Mechanism of the Temperature Effect on PEO-PPO-PEO Aqueous Solutions. The "molecular-level" mechanism behind the temperature dependence of PEO-PPO-PEO micellization, and particularly the effect of PEO, is still a matter of some controversy. In principle, models in the literature are based on either the solute–solvent[67,68] or the solute–solute interactions.[69] Kjelander and Florin[67] attempted to reproduce the negative entropy and enthalpy of water–PEO mixing and the phase diagram of the PEO–water system assuming a zone with increased structuring of water to exist around the PEO chain. The phase separation that takes place at high temperatures was attributed to a breakdown of the zones of enhanced water structure. The chain length dependence was mainly determined from the combinatorial entropy of the chains. The water solubility of PEO could be explained in terms of a good structural fit between the water and the polymer. While PPO also has negative entropy and enthalpy of mixing with water, they are less negative than those for PEO–water. Kjelander and Florin[67] claim that, when PPO is introduced into water, it also develops a hydration shell with an enhanced structure of water, but since the methyl groups of PPO constitute a steric hinderance, the water structure is weak and leads to phase separation. It should be noted here that, while PPO is practically insoluble in water at room temperature, it can be soluble at low temperatures (e.g., up to −7 °C for PPO with degree of polymerization = 20, reported in ref 67).

A weak point to the above theory, according to Karlstrom,[69] is the highly disordered state of PEO in aqueous solutions that is incompatible with an ordered water hydration shell. Karlstrom[69] predicted (with semiquantitative agreement) the phase diagram of PEO–water using Flory–Huggins theory and assuming that each segment of the PEO chain may exist in two forms due to the rotations around the C–C and C–O bonds. From quantum mechanical calculations, corroborated by ^{13}C NMR chemical shift measurements, the conformation of the OCCO segment was divided into two classes, one being polar, having a low energy and a low statistical weight, and one being less polar, or nonpolar, having a higher energy and a higher statistical weight.[14] At low temperatures, the former class of states dominates and the solute–solvent interaction is favorable, whereas at higher temperature, the latter class of states becomes increasingly populated, rendering the solute–solvent interaction less favorable. Malmsten and Lindman[14] used a similar model, assuming temperature-dependent EO–EO, PO–PO, and EO–PO interactions, to predict the micellization behavior of PEO-PPO-PEO block copolymer solutions. They found that both PO and EO blocks repel each other progressively less with increasing temperature until, at some temperature, the effective PO–PO attraction dominates over the EO–EO repulsion and micelles form. A more comprehensive discussion of the mechanisms of the temperature dependence, and clouding in particular, is presented by Carlson et al.[70]

The self-consistent mean-field lattice models used for predicting PEO-PPO-PEO block copolymer solution behavior by Hurter et al.[28] and Linse et al.[71] also incorporated Karlstrom's ideas and accounted for conformational distributions in PEO and PPO, thus allowing the investigation of temperature effects on the aggregation behavior of these copolymers. The model predictions of refs 28 and 71 (e.g., decrease of the cmc and cmt with increasing PPO) agree well with the trends observed experimentally, thus supporting the polar–nonpolar state model as an explanation of the temperature effect on the solution behavior of PEO and PPO.

Conclusions

The critical micellization temperature and critical micellization concentration values of 12 Pluronic poly-

(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO-PPO-PEO) block copolymers, covering a wide range of molecular weights (2900–14 600) and PPO/PEO ratios (0.19–1.79), have been determined employing a dye solubilization method. In general, it is evident that copolymers with a larger hydrophobic (PPO) domain formed micelles at lower concentrations or, for a given copolymer concentration, have lower cmt's. For copolymer groups with the same PPO/PEO ratio, Pluronics of higher molecular weight form micelles more readily, e.g., at lower concentrations and temperatures. The hydrophilic group appears to play a smaller role in the micellization process.

A closed association model was found to describe adequately the copolymer micellization process for the majority of the Pluronics and was used to obtain standard free energies ($\Delta G°$), enthalpies ($\Delta H°$), and entropies ($\Delta S°$) of micellization for these Pluronics. The standard enthalpy of micellization, $\Delta H°$, was found to be positive for all Pluronics tested, indicating that the transfer of unimers from solution to the micelle is an enthalpically unfavorable endothermic process. A negative entropy contribution must, therefore, be the driving force for the micellization for the block copolymers.

The comprehensive compilation of cmt and cmc data for aqueous Pluronic solutions presented here is expected to be a value in the numerous applications of Pluronics that depend on their micelle forming abilities. The utility of these results is enhanced by the finding that the free energies of micellization per monomer unit, $\Delta G°/(N_{\mathrm{EO}} + N_{\mathrm{PO}})$, correlated well with molecular weight and solution concentration over the wide range of polymer composition ratios investigated and can be used for the estimation of the micellization parameters of other polymers in this class. The basis for this correlation is as yet unclear, but it probably reflects a decoupling of the importance of the ether oxygens in determining the polymer–solvent and polymer–polymer interactions and the entropic penalties associated with confining the polymer chain within the micelles.

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