TABLE 13.2
Comparison in Micellar Parameters between 17R4 and L-64 Micelles in Water

	Pluronic L-64	Pluronic 17R4
Composition	$(EO)_{13}(PO)_{30}(EO)_{13}$	$(PO)_{14}(EO)_{24}(PO)_{14}$
HLB value	15	7–12
CMC at 40°C, g/mL	9.0×10^{-14}[a]	9.1×10^{-2}
*M*w, g/mol	2.8×10^{5}[a]	2.65 × 104 (40.0°C)
Aggregation number	88 (42.5°C)[b]	10 (40.0°C)
A_2, $cm^3 mol\ g^{-2}$	~6.0×10^{-4} (42.5°C)[b]	~6.0×10^{-5}
R_h, nm	10.2 (42.5°C)[b]	4.0 (40.0°C)
$\Delta H°$, kJ/mol	210	115
$\Delta G°$, at 40.0°C, kJ/mol	–21	–9
$\Delta S°$, at 40.0°C, kJ/(mol K)	0.74	0.40

Source: Zhou, Z. and Chu, B., *Macromolecules*, 27, 2025–2033, 1994.
Note: *M*w is the weight-average molecular weight, A_2 the second virial coefficient, R_h, hydrodynamic radius.
[a] Reddy, N.K. et al., *J. Chem. Soc.*, *Faraday Trans.*, 86, 1569–1572, 1990.
[b] Zhou, Z. and Chu, B., *Macromolecules*, 21, 2548–2554, 1988a.

Linse (1993) compared the micellization behavior of an ABA triblock copolymer (PEO-*b*-PPO-*b*-PEO) with a BAB triblock copolymer (PPO-*b*-PEO-*b*-PPO) with the same composition as that of Pluronic P-105 (i.e., $(EO)_{74}(PO)_{56}$). He concluded that PPO-*b*-PEO-*b*-PPO forms micelles only within a narrow temperature range and only at high concentrations. However, the CMC value of Pluronic P105 is a factor of two lower than that of the PPO-*b*-PEO-*b*-PPO copolymer. It was predicted that the PPO-*b*-PEO-*b*-PPO forms larger micelles than P105. Additional studies of other BAB triblock copolymers can be found elsewhere (Mortensen et al., 1994; Yekta et al., 1995; Yang et al., 1996; Zhou et al., 1996).

Temperature and Concentration Effects on Solubilization

In investigating temperature effects on drug solubilization in micellar systems, changes in the micellar properties as well as those in the aqueous solubility of the solute significantly affect the solubilization of the solute. As discussed in the "Temperature and Concentration Effects on Micellization" section, the CMC values decrease with increasing temperature in line with an inverse temperature-surfactant solubility relationship. In the case of PEO surfactants, the aqueous solubility of the surfactants is attributed to hydrogen bonding between the ether oxygens of EO chains and water molecules. When the temperature is increased, these hydrogen bonds break and the hydrophilicity of the PEO chain is reduced, rendering the surfactant less soluble so that micellization occurs at a lower concentration (Almgren et al., 1995). This suggests that the solubilization of a solute will occur at lower surfactant concentrations, and the solubilization capacity increases per gram of surfactant in solution, owing to the decrease of CMC caused by an increase in the temperature. In addition, micelles of polymeric surfactants rapidly grow in size with increasing temperature, which may be in part due to greater hydrophobicity of the monomer and geometric considerations. Therefore, in general, the higher the temperature, the larger the micellar solubilization capacity for a solute.

Lin and Yang (1987) found that the diazepam solubilizing capacities of Pluronics increased with increasing temperature and rank in the order: F-68 < F-88 < F-108. These results, along with partition coefficient (K_m) values, are shown below in Table 13.3. The higher the K_m, the greater the amount of diazepam entrapped within the micelles. The difference in K_m values at different temperatures is because micellar solubility increases more rapidly with temperature than does the solubility in water. The rise in solubility of diazepam in the presence of Pluronic