surfactants, for example, surfactants with bulky, rigid hydrophobic portions, such as bile salts that have a very broad concentration range of micellization. These surfactants also show variations in the monomer concentration above the CMC, and thus the CMC is not indicative of a critical phenomenon.

The following two items need to be considered from a practical perspective, especially for ionic surfactants, when measuring the CMC of surfactants (Constantinides and Steim, 1985): (a) surface-active impurities in commercial surfactants, such as SDS, give rise to a minimum in the surface tension–concentration plot, and unless a highly purified surfactant is used an approximate value of the CMC is obtained, and (b) in the dye solubilization method, it is important that the dye and the surfactant are of the same charge, to avoid premicellar association, that is, salt formation between the dye and the surfactant below the true CMC of the surfactant.

Micellar Size and Aggregation Number (*n*)

The second important characteristic of the micellar solution that relates to solubilization is the micelle size. Poor aqueous-soluble compounds are solubilized either within the hydrocarbon core of the micelle or, very commonly, within the head group layer at the surface of the micelle or in the palisade portion of the micelle. Predictions of the micelle size have relied on the use of empirical relationships employed within a thermodynamic model, for instance the law of mass action where micellization is in equilibrium with the associated and unassociated (monomer) surfactant molecules (Attwood and Florence, 1983).

The number of monomers that come together to form a micelle is called the aggregation number. Owing to the dynamic nature of micelles, this number represents a model of the micellar composition over a period of time. The aggregation number is calculated by dividing the micellar molecular weight by the molecular weight of the surfactant monomer. Micellar molecular weight may be determined by numerous methods, such as light scattering, sedimentation equilibrium, dynamic light scattering, and small-angle X-ray scattering. Micellar size is sensitive to the same experimental conditions as the CMC, including pH, temperature, ionic strength, and the presence of additives (Myers, 1992). The aggregation number for a particular surfactant may only be valid within a certain concentration range. Aggregation numbers for various surfactant types are given in Table 12.1. A few generalizations can be made about the aggregation number:

TABLE 12.1
Aggregation Numbers for Surfactants in Water

Surfactant	Temperature (°C)	Aggregation Number
$C_{10}H_{21}SO_3^-$	30	40
$C_{12}H_{25}SO_3^-Na^+$	40	54
$(C_{12}H_{25}SO_3^-)Mg^{2+}$	60	107
$C_{12}H_{25}SO_4^-Na^+$	23	71
$C_{14}H_{29}SO_3^-Na^+$	60	80
$C_{12}H_{25}N(CH_3)^+Br^-$	23	50
$C_8H_{17}O(CH_2CH_2O)_6H$	30	41
$C_{10}H_{21}O(CH_2CH_2O)_6H$	35	260
$C_{12}H_{25}O(CH_2CH_2O)_6H$	15	140
$C_{12}H_{25}O(CH_2CH_2O)_6H$	25	400
$C_{12}H_{25}O(CH_2CH_2O)_6H$	35	1400
$C_{14}H_{29}O(CH_2CH_2O)_6H$	35	7500

Source: Taken from Myers, D., Micellization and association, in *Surfactant Science and Technology*. 2nd ed., D. Myers (Ed.), VCH Publishers, New York, 1992.