

**TABLE 12.8**  
**Micellar Solubilization and Other Physicochemical Parameters for Binary Mixed Surfactant Systems**

| Solute     | Mixed Surfactant                                     | $\beta$ | $\theta N$ | $\theta K_m$ |
|------------|--|---------|------------|--------------|
| Benzene    | NaPFO + NaDEC  | 1.8     | +          | +            |
| 1-Pentanol | NaPFO + NaDEC  | 1.8     | +          | -            |
| 1-Octanol  | DMLL + C <sub>12</sub> Na                            | -15     | +          | +            |
| 1-Octanol  | DMLL + C <sub>14</sub> Br                            | -1      | -          | -            |
| 1-Hexanol  | C <sub>16</sub> PyCl + NPE <sub>15</sub>             | -1.3    | NA         | -            |
| 1-Hexanol  | C <sub>12</sub> Cl + C <sub>12</sub> Na              | -25     | +          | -            |
| 1-Pentanol | C <sub>10</sub> Na + C <sub>10</sub> Br              | -13.2   | +          | -            |
| 1-Pentanol | C <sub>12</sub> E <sub>23</sub> + C <sub>12</sub> Na | -2.6    | 0          | -            |
| 1-Pentanol | LiPFO + C <sub>12</sub> Li                           | 2.2     | +          | +            |
| 1-Decane   | C <sub>12</sub> Cl + C <sub>12</sub> Na              | -25     | +          | +            |
| 1-Hexane   | NPE <sub>10</sub> + C <sub>16</sub> PyCl             | -1.3    | NA         | +            |
| 1-Hexane   | NPE <sub>10</sub> + C <sub>12</sub> Na               | -4.8    | NA         | +            |
| 1-Hexane   | C <sub>16</sub> PyCl + C <sub>12</sub> Na            | -25     | NA         | +            |

NaPFO, sodium perfluorooctanoate; NaDEC, sodium decanoate; DMLL, *N*<sup>α</sup>, *N*<sup>ε</sup>-dimethyl-*N*<sup>ε</sup>-lauroyl lysine; LiPFO, lithium perfluorooctanesulfonate; NPE<sub>10</sub>, nonylphenolpoly(oxyethylate); C<sub>16</sub>PyCl, hexadecylpyridinium chloride; NA, not available.

Additional values of  $\beta$  have been tabulated for many binary surfactant mixtures (Rosen, M. J., *Surfactants and Interfacial Phenomena*, 2nd ed., Wiley, New York, 1978).

Source: Taken from Treiner, C. et al. *Langmuir*, 6, 1211–1216, 1990.

solutes, there was an increase in the micellar aggregation number on surfactant mixing for anionic/nonionic mixtures. However, this increase is not responsible for micellar solubilization changes of polar solutes. Furthermore, the structural changes should have little effect on the micellar solubilization of polar solutes that interact with the micelle by surface adsorption.

Others have studied the volumetric changes occurring in mixed micelles of anionic–anionic and nonionic–nonionic surfactants as a determinant of intermolecular interactions and a measure of the thermodynamic ideality of mixing. In particular, Funasaki et al. (1986) have studied the volumetric behavior of mixed micelles of ionic and nonionic surfactants and analyzed their results in terms of regular solution theory. They found that in water, anionic surfactants such as SDS bind to PEG, but cationic surfactants (such as DTAB) do not, likely due to differences observed in  $\Delta V_m$ . For two surfactants, the micelle has a smaller volume than the liquid. Even highly charged anionic surfactant mixtures such as esters of coenzyme A (CoA) with fatty acids (palmitic, stearic, and oleic) can be described using regular solution theory (Constantinides and Steim, 1988). The behavior of the palmitoyl-CoA/stearoyl-CoA mixture is ideal, while the palmitoyl-CoA/oleoyl-CoA mixture, although not exhibiting ideal behavior, can be fitted reasonably well by nonideal theory. In both mixtures, selective micellization takes place and, unlike the case of pure fatty acyl-CoAs, above the CMC of the mixtures the concentration of free molecules in solution is strongly dependent on total concentration (Constantinides and Steim, 1988). The regular solution theory approach has also been extended to multicomponent surfactant mixtures, by decomposing the interactions into pair-wise interactions between every possible surfactant pair.

In spite of the wide use and convenience of regular solution theory, the theoretical validity of using it to describe nonideal mixing in mixed surfactant micelles has been questioned (Hoffmann and Poessnecker, 1994). Regular solution theory assumes that the excess entropy of mixing is zero; calorimetric measurements or calculations of the enthalpy of mixing combined with mixture CMC