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SHORT COMMUNICATION

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Mixed micelle behavior of poly(ethylene glycol) alkyl ethers with series of monomeric cationic, phosphonium cationic, and zwitterionic surfactant

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Abstract The steady state fluorescence measurements have been carried out for the binary mixtures of poly (ethylene glycol) alkyl ethers (C_iE_j) with series of monomeric cationic (MC), zwitterionic (ZI), and phosphonium cationic (PC) surfactants over the whole mole fraction range by using pyrene as fluorescence probe. The cmc values for all the binary mixtures, thus, determined have been further evaluated by using the regular solution theory. The various micellar parameters such as regular solution interaction parameter (β), micropolarity (I_1/I_3), and mean micelle aggregation number (N_{agg}) have been determined. A strong influence of hydrophobicity of both nonionic as well as cosurfactant (CS) components has been observed on the nature of mixed micelles. The presence of bulky head groups of PC surfactants significantly contributes towards the unfavorable mixing.

Keywords Mixed micelles · Nonionic surfactants · Fluorescence studies · Micropolarity · Aggregation number

Introduction

Poly(ethylene glycol) alkyl ethers are typical nonionic surfactants with general chemical structure, $H(CH_2)_i(OCH_2CH_2)_jOH$, which is simply denoted by C_iE_j, where i refers to the number of carbon atoms in the hydrocarbon chain and j to the number of oxyethylene units in the molecule. The aqueous mixtures of this class of surfactants form a variety of mesomorphic phases depending on the composition and temperature. It also allows the flexibility in changing the magnitude of hydrophilic interactions by varying the number of oxyethylene units, which are mainly responsible for its solubilization in aqueous phase. The aqueous C_iE_j mixtures have attracted considerable attention for many years both from the academic as well as practical interests [1–12]. These surfactants are highly surface active and show micellization at very low concentration range, i.e., from 10^{-5} to 10^{-4} mol dm^{-3}. Their cmc value depends on number of ether oxygens; increase in this number increases the cmc. The properties of these surfactants can be modified considerably by simply changing the length of polyoxyethylene group. These surfactants are well suited for mixing and formulation with a variety of other surfactants, because they are chemically inert and stable towards pH change; hence, they have been extensively used in the cosmetic industry. Though extensively studied, they still lack a quantitative interpretation of their mixed micellar behavior with CS (such as cationic, zwitterionic, and Gemini) as far as their hydrophobicity and CS head group effects are concerned. The present study has been undertaken in this direction so as to evaluate the mixing properties of such combinations to achieve their appropriate industrial uses.

Experimental

Materials

Octaethyleneglycol mono-*n*-decylether ($C_{10}E_8$), tetraethyleneglycol mono-*n*-dodecylether ($C_{12}E_4$), and octaethyleneglycol mono-*n*-tetradecylether ($C_{14}E_8$) were obtained from TCI, Japan. The monomeric cationic (MC) surfactants such as dodecyl- (DTAB), tetradecyl- (TTAB), and

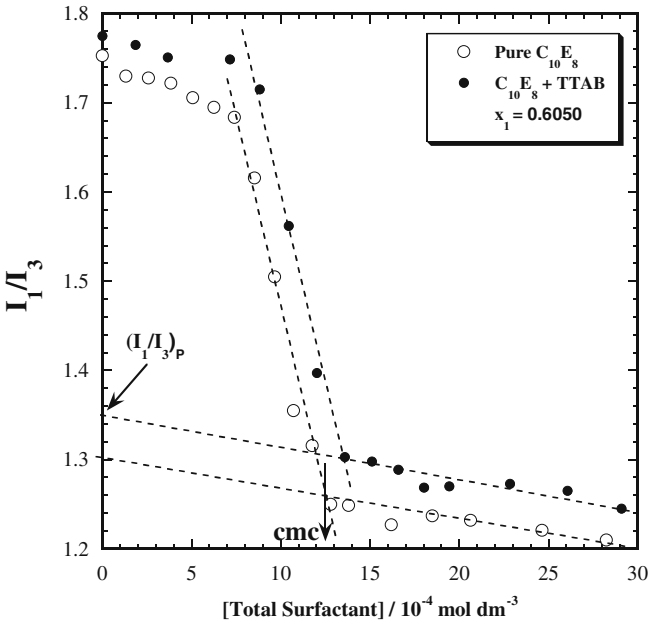


Fig. 1 Variation of the pyrene intensity I_1/I_3 ratio with the total surfactant concentration of pure $C_{10}E_8$ (○) and $C_{10}E_8$+TTAB (●) in water at 25 °C; the *vertical arrows* denotes the cmc values

Table 1 Values of critical micelle concentrations (cmc/10^{-4} mol dm^{-3}) for nonionic surfactants and cosurfactants from fluorescence measurements at 25 °C

Surfactants	cmc	Literature values
$C_{10}E_8$	11.1	11.5 [22]
$C_{12}E_4$	0.95	0.64 [23]
$C_{14}E_8$	0.33	–
DTAB	160	152 [24], 160 [25]
TTAB	38.0	38.3 [24]
HTAB	10.0	10.0 [24]
DPS	35.0	37.0 [25]
TPS	3.70	–
HPS	0.79	–
DeTPB	11.5	–
TTPB	7.1	7.7 [26]
HTPB	1.2	1.1 [26]

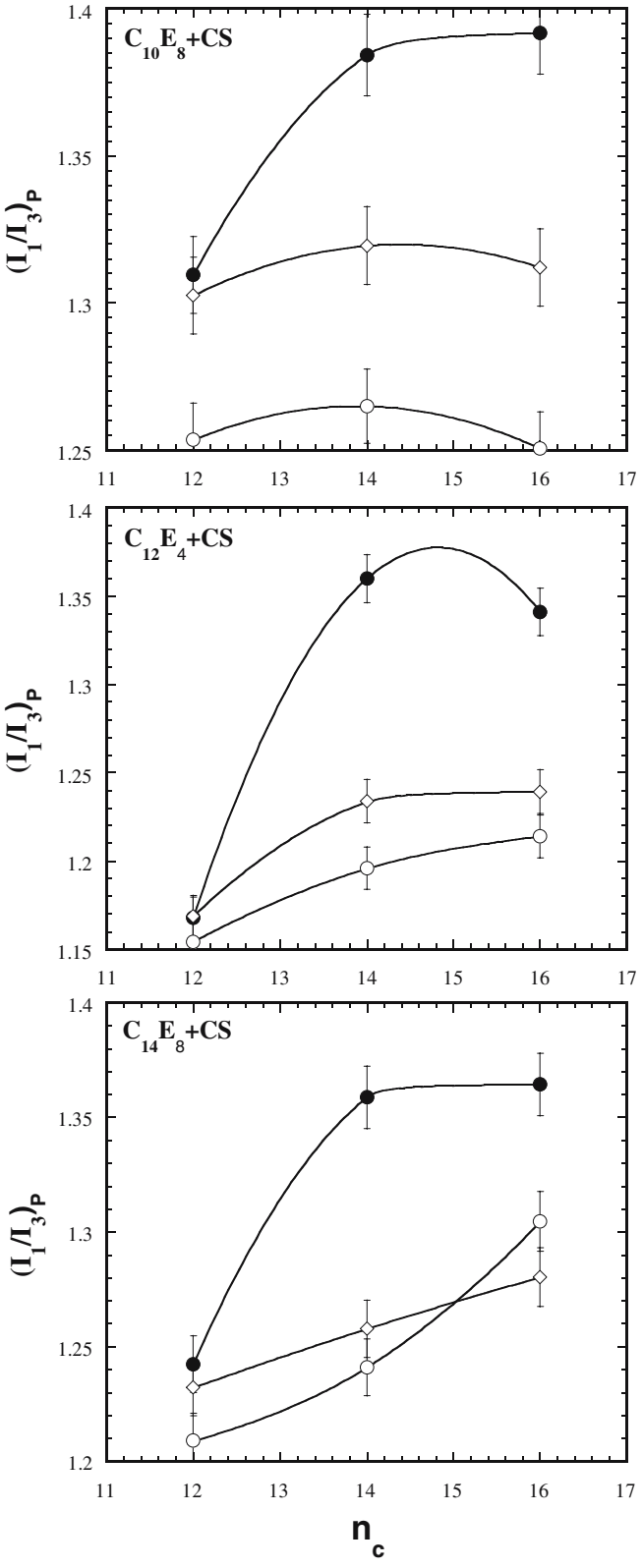
hexadecyltrimethylammonium (HTAB) bromides were obtained from Lancaster Synthesis, UK. The zwitterionic surfactants (ZI) like 3-(*N*,*N*-dimethyldodecylammonio propane) sulfonate (DPS), 3-(*N*,*N*-dimethyltetradecylammonio propane) sulfonate (TPS), and 3-(*N*,*N*-dimethylhexadecylammonio propane) sulfonate (HPS), all more than 99% pure, were procured from Flüka. The phosphonium cationic (PC) surfactants such as decyltriphenylphosphonium bromide (DeTPB), tetradecyltriphenylphosphonium bromide (TTPB), and hexadecyltriphenylphosphonium bromide (HTPB) were obtained from Lancaster Synthesis, UK. Pyrene was obtained from Aldrich and quencher, hexadecylpyridinium chloride (HPyCl), was procured from Lancaster Synthesis, UK. The MC and PC surfactants were used after purification from ethanol while all other reagents were used as received. Water was purified by deionization followed by double distillation. The solutions were prepared by mass with an accuracy of 0.01 mg. All the measurements have been performed at 25 °C after giving sufficient time for stabilization.

Method

The pyrene fluorescence of the mixtures of a series of MC, ZI, and PC with C_iE_j has been measured by using Hitachi 2,500 fluorescence spectrophotometer at 25 °C. It is well known that the ratio of first to third vibronic peaks (I_1/I_3) of pyrene emission spectrum at 385 nm indicates the polarity of the medium in which it is dissolved. The excitation wavelength of pyrene was, λ=335 nm and the pyrene concentration was around 10^{-6} mol dm^{-3}. For the fluorescence measurements, stock solutions of two unlike components of various binary mixtures were prepared by dissolving appropriate amounts of each component. In this solution, required amount of pyrene was added and kept for overnight stirring to ensure the complete solubilization of pyrene in the micellar phase. Fluorescence titrations were performed by successive additions of concentrated stock solutions to reference solution (i.e., water plus pyrene) to keep the pyrene concentration constant.

Table 2 Values of average interaction parameter, β_{avg}, for the mixtures of nonionic and cosurfactants from fluorescence measurements at 25 °C

Systems	β_{avg}	Systems	β_{avg}	Systems	β_{avg}
$C_{10}E_8$ + DTAB	2.1	$C_{10}E_8$ + DPS	3.0	$C_{10}E_8$ + DeTPB	−0.2
$C_{10}E_8$ + TTAB	−0.4	$C_{10}E_8$ + TPS	1.4	$C_{10}E_8$ + TTPB	−1.0
$C_{10}E_8$ + HTAB	−1.0	$C_{10}E_8$ + HPS	−1.6	$C_{10}E_8$ + HTPB	–
$C_{12}E_4$ + DTAB	–	$C_{12}E_4$ + DPS	–	$C_{12}E_4$ + DeTPB	–
$C_{12}E_4$ + TTAB	−1.4	$C_{12}E_4$ + TPS	3.7	$C_{12}E_4$ + TTPB	3.2
$C_{12}E_4$ + HTAB	−0.4	$C_{12}E_4$ + HPS	2.5	$C_{12}E_4$ + HTPB	2.3
$C_{14}E_8$ + DTAB	–	$C_{14}E_8$ + DPS	–	$C_{14}E_8$ + DeTPB	–
$C_{14}E_8$ + TTAB	–	$C_{14}E_8$ + TPS	3.0	$C_{14}E_8$ + TTPB	–
$C_{14}E_8$ + HTAB	9.0	$C_{14}E_8$ + HPS	1.1	$C_{14}E_8$ + HTPB	8.0



◀ **Fig. 2** Plot of polarity index, $(I_1/I_3)_P$ vs n_C in the hydrophobic tail of CS of **a** $C_{10}E_8$ + MC, $C_{10}E_8$ + ZI, and $C_{10}E_8$ + PC; **b** $C_{12}E_4$ + MC, $C_{12}E_4$ + ZI, and $C_{12}E_4$ + PC; **c** $C_{14}E_8$ + MC, $C_{14}E_8$ + ZI, and $C_{14}E_8$ + PC. *Empty circles* for $C_{10}E_8/C_{12}E_4/C_{14}E_8$ + MC; *filled circles* for $C_{10}E_8/C_{12}E_4/C_{14}E_8$ + PC; *empty diamonds* for $C_{10}E_8/C_{12}E_4/C_{14}E_8$ + ZI

Results and discussion

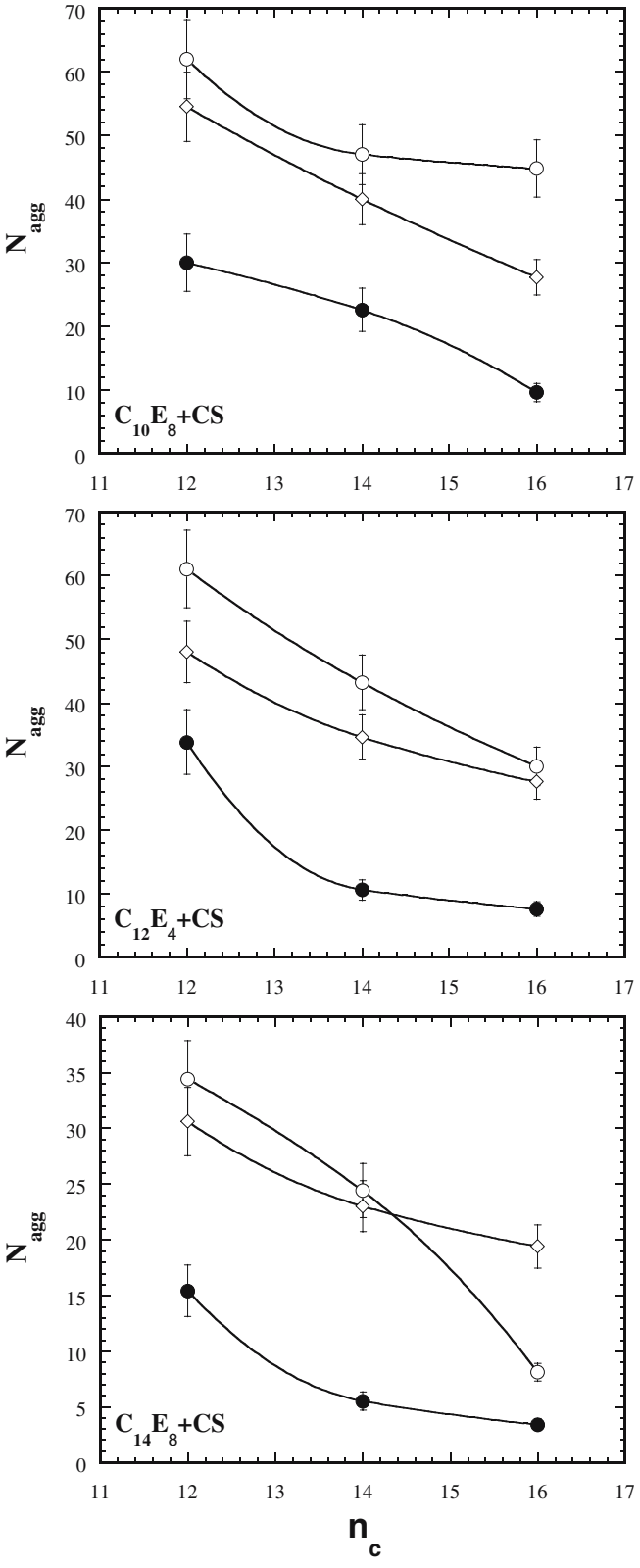
The mixed micelle formation of various binary mixtures of C_iE_j + monomeric cationic (MC), C_iE_j + zwitterionic (ZI), and C_iE_j + phosphonium cationic (PC) have been carried out in pure water. A variation in the I_1/I_3 value of pyrene fluorescence clearly shows the micelle formation process, which is demonstrated by a decrease in I_1/I_3 ratio upon the micelle formation and then tending to a constant value. A break in the I_1/I_3 curve represents the critical micelle concentration (cmc) in each case (Fig. 1). These values for the pure components have been listed in Table 1 and compared with those available in the literature. A good agreement can be observed between the present and reported values. Previous studies [13–15] have shown that the mixed micelle formation with nonionic surfactants with ionic ones generally takes place due to the attractive interactions between the unlike monomers of two components. The origin of such interactions mainly attributed to the reduction in polar head group repulsions upon the incorporation nonionic surfactant moiety [16]. In view of this fact, the choice of present CS with bulky head groups specifically lies to understand this effect. This results have been quantitatively analyzed on the basis of regular solution theory (RST) [17], which allows us to evaluate the interaction parameter (β) among the unlike monomers of two components in a binary surfactant mixture by using the following equations:

$$\frac{X_1^2 \ln\left(x_1 cmc / X_1 cmc_1\right)}{(1-X_1)^2 \ln\left[(1-x_1)cmc/(1-X_1)cmc_2\right]} = 1 \tag{1}$$

and

$$\beta = \frac{\ln\left(\frac{cmc x_1}{cmc_1 X_1}\right)}{(1-X_1)^2} \tag{2}$$

Where cmc_1, X_1, and x_1, are the critical micelle concentration, micelle, and bulk mole fractions of CS; and cmc is the value of mixed surfactants. The average values of interaction parameter (β_{avg}), thus, obtained from Eq. 2, are listed in Table 2. All columns of Table 2 show that the β_{avg} values are predominantly positive and even become significantly positive as we move from $C_{10}E_8$ to $C_{14}E_8$ mixtures, i.e., increasing hydrophobicity of the nonionic component. It means that the increase in hydrophobicity brings a positive contribution to β_{avg} value, and under the



◀ **Fig. 3** Plot of aggregation number, N_{agg} vs n_C in the hydrophobic tail of CS of **a** $C_{10}E_8$ + MC, $C_{10}E_8$ + ZI, and $C_{10}E_8$ + PC; **b** $C_{12}E_4$ + MC, $C_{12}E_4$ + ZI, and $C_{12}E_4$ + PC; **c** $C_{14}E_8$ + MC, $C_{14}E_8$ + ZI, and $C_{14}E_8$ + PC. *Empty circles* for $C_{10}E_8/C_{12}E_4/C_{14}E_8$ + MC; *filled circles* for $C_{10}E_8/C_{12}E_4/C_{14}E_8$ + PC; *empty diamonds* for $C_{10}E_8/C_{12}E_4/C_{14}E_8$ + ZI

framework of regular solution theory this represents an increase in the antagonistic behavior. These results further suggest that although negative contribution of β_{avg} was expected in these nonionic + ionic binary mixtures (and indeed some of them with $C_{10}E_8$ show the negative β_{avg} values), the presence of mainly positive β_{avg} values at higher hydrophobicities of C_iE_j both and CS indicate the unfavorable mixing. The folding of longer hydrophobic tail seems to create the screening of reduction in polar head group repulsions and thereby, leading to the antagonistic mixing behavior. Unlike the ionic surfactants, the nonionic head groups (i.e., polyoxyethylene) do not possess specific confined space, and hence, a folding of longer hydrophobic tail of CS is expected to bring some of the methylene groups in close proximity of polyoxyethylene groups. Rosen and Zhou [18, 19] have also mentioned that the relative strength of interactions at the interface of ionic-POE nonionic mixtures are determined by the branching and bulkiness of hydrophobic and hydrophilic groups. The increase in both latter factors reduces these interactions.

Micropolarity

To evaluate the microenvironment of the mixed micelles, the polarity index, $(I_1/I_3)_P$, of pyrene solubilized in the interior of the micelle has been studied. This value can be computed by extrapolating I_1/I_3 values in the postmicellar region to zero total surfactant concentration as shown in Fig. 1. The $(I_1/I_3)_P$ at equimolar ratio vs number of carbon atoms (n_C) in the hydrophobic tail of the CS component have been plotted in Fig. 2. One can see that the variation of $(I_1/I_3)_P$ for all binary mixtures of C_iE_j with various CS is almost identical to each other (Fig. 2a,c). The $(I_1/I_3)_P$ mainly shows an increase with the increase in n_C from C_{12} to C_{14} and then tending to level off at C_{16} in most of the cases. It means that the increase in hydrophobicity of CS increases the polarity of the medium in which pyrene solubilized. Though pyrene is predominantly hydrophobic in nature due to the presence of aromaticity, the solubilization site of pyrene, thus, remains in the palisade layer. In a micelle, the palisade layer lies next to the Stern layer towards the core and hence, relatively less hydrophobic in comparison to that of core. Thus, the polarity index shown in Fig. 2 is in fact the microenvironment sensed by pyrene solubilized in the palisade layer. Therefore, increase in $(I_1/I_3)_P$ with respect to an increase in n_C gives direct information regarding a decrease in the hydrophobic environment.

A close inspection of Fig. 2 also suggests that the overall $(I_1/I_3)_P$ for various series of binary mixtures increases in the order of C_iE_j + MC < C_iE_j + ZI < C_iE_j + PC. There is also little increase in the polarity index for C_iE_j + MC with

respect to an increase in n_C in comparison to a large increase in the case C_iE_j + PC. This is due to the fact that the head group of PC surfactant occupies large surface area because it possesses three phenyl rings in comparison to that of MC. The MC surfactants have only methyl groups instead of phenyl groups. Such a large PC head group should occupy large surface area in the Stern layer of the mixed micelles and would result in an increase in the hydration of the Stern layer of PC micelle in comparison to that of MC. Thus, an increase in the hydration of the Stern layer would obviously increase the polarity and would be sensed by pyrene residing in the adjoining palisade layer. That is why the polarity index is maximum for the binary mixtures of PC and minimum for MC. The increase in the n_C value is expected to further enhance this effect due to the folding of hydrophobic tail, which would create more space and, hence, allow more water molecules to accommodate.

Mean micelle aggregation number

The mean micelle aggregation number has been determined by using HPyCl as a quencher along with pyrene. The quenching of fluorescence of pyrene by HPyCl has been utilized to find out N_{agg} [20, 21] by using the following equation.

$$N_{agg} = \left(\frac{\ln (I_o/I)}{[Q]}\right)\{([CS] + [C_iE_j]) - cmc\} \quad (3)$$

where I_o and I are the fluorescence intensities in the absence and presence of quencher (Q), cmc is the value obtained from Fig. 1 for both single and mixed systems. All N_{agg} measurements for various binary mixtures of equimolar ratios were carried out by mixing concentrated surfactant solution ([surf] = 10×cmc) of two unlike components and have been plotted in Fig. 3a,c. All plots of these figures represent a gradual decrease in N_{agg} value with increase in n_C. In some cases of C_iE_j + PC mixtures, the N_{agg} values are even less than 10, which do not bear any physical significance and have only been shown for comparison purposes. The overall variation suggests an essential decrease in N_{agg} in the order of C_iE_j + MC > C_iE_j + ZI > C_iE_j + PC among all binary mixtures. It is to be noted that this order is exactly opposite to that represented by the variation of polarity index shown in Fig. 2. It means that the increase in polarity index with respect to an increase in n_C in each case practically reduces the N_{agg}, or in other words the mixtures with higher polarity index show smaller N_{agg}. Hence, the increase in polarity of the Stern layer or decrease in the hydrophobicity of the palisade layer in fact is responsible for a decrease in N_{agg}. Therefore, an increase in the polarity and decrease in the N_{agg} with respect to an increase in n_c or increase in the bulkiness of the ionic head group will reduce the synergism and lead to antagonism.

Conclusions

The following conclusions can be drawn from this study:

(1) The presence of bulky polar head groups (i.e., of phosphonium surfactants) increases the polarity of palisade layer of the mixed micelles in comparison to that of ammonium head groups. Such an increase in the polarity of the Stern layer reduces the hydrophobic environment of the mixed micelles and thereby decrease the mean micelle aggregation number.
(2) The above-mentioned effect further increases with the increase in hydrophobicity of CS and has been attributed to the screening of polar head group repulsions.

References

1. Kunieda H, Shigeta K, Ozawa K, Suzuki M (1997) J Phys Chem B 101:7952
2. Mulley BA, Metcalf AD (1964) J Colloid Interface Sci 19:501
3. Lang JC, Morgan RD (1980) J Chem Phys 73:5849
4. Mitchell DJ, Tiddy GJT, Waring L, Bostock T, McDonald MP (1983) J Chem Soc Faraday Trans 1(79):975
5. Adam CD, Durrant DJ, Lowry MR, Tiddy GJT (1984) J Chem Soc Faraday Trans 1(80):789
6. Andersson B, Olofsson G (1987) Colloid Polym Sci 265:318
7. Strey R, Schomäcker R, Roux D, Nallet F, Olsson U (1990) J Chem Soc Faraday Trans 1(86):2253
8. Kratzat K, Guittard F, de Givenchy ET, Cambon A (1996) Langmuir 12:6346
9. Nibu Y, Inoue T (1998) J Colloid Interface Sci 205:231
10. Nibu Y, Inoue T (1998) J Colloid Interface Sci 205:305
11. Chernik GG (2000) Curr Opin Colloid Interface Sci 4:381
12. Kratzat K, Finkelmann H (1996) J Colloid Interface Sci 181:542
13. Misselyn-Bauduin AM, Thibaut A, Grandjean J, Broze G, Jerome R (2000) Langmuir 16:4430
14. Bergstrom M, Eriksson JC (2000) Langmuir 16:7173
15. Zhou Q, Rosen MJ (2003) Langmuir 19:4555

16. Rubingh DN (1979) Solution chemistry of surfactants. In: Mittal KL (ed) 1979 Plenum, New York, 1:337
17. Golub TP, de Keizer A (2004) Langmuir 20:9506
18. Rosen MJ, Zhou Q (2001) Langmuir 17:3532
19. Rosen MJ, Zhou Q (2003) Langmuir 19:4555
20. Turro NJ, Gratzel M, Braun AM (1980) Angew Chem Int Ed Engl 19:675
21. Malliaris A (1987) Progr Colloid Polym Sci 73:161
22. Richard DC, Johan BC (2003) J Colloid Interface Sci 260:244
23. Rosen MJ, Cohen A, Dahanayaka M, Hua X (1982) J Phys Chem 86:541
24. Carnero Ruiz C, Aguiar J (2000) Langmuir 16:7946
25. MJ Rosen (1989) Surfactants and interfacial phenomena, 2nd edn. Wiley, New York
26. Prasad M, Moulik SP, MacDonald A, Palepu R (2004) J Phy Chem B 108:355