Colloid Polym Sci (2005) 283: 671–676
DOI 10.1007/s00396-004-1204-2

ORIGINAL CONTRIBUTION

Mandeep Singh Bakshi
Shweta Sachar

Interactions of monomeric and dimeric cationic surfactants with anionic polyelectrolytes: a fluorescence study

Received: 21 May 2004
Accepted: 28 July 2004

M. S. Bakshi (✉) · S. Sachar
Department of Chemistry,
Guru Nanak Dev University,
Amritsar, Punjab, 143005, India

Abstract The interactions of conventional cationic, i.e. dodecyl-(DTAB), tetradecyl-(TTAB), and hexadecyltrimethylammonium bromides (HTAB), and dimeric cationic surfactants, i.e. dimethylene bis decyl-(10-2-10), and dodecyldimethylammonium bromides (12-2-12) with anionic polyelectrolytes, were studied by fluorescence measurements. The variation of I_1/I_3 ratio of the fluorescence of pyrene in aqueous solutions of polyelectrolytes was measured as a function of surfactant concentration. A three-step aggregation process involving the critical aggregation concentration (cac) and critical micelle concentration (cmc) was observed in each case. The cationic surfactants with lower hydrophobicity demonstrated higher degree of binding and vice versa.

Keywords Cationic surfactants · Anionic polyelectrolytes · Fluorescence measurements · Critical aggregation concentration

Introduction

Interactions between polymers and surfactants in aqueous solutions have been intensively investigated in the past few decades due to the numerous technological and industrial applications as well as from the fundamental standpoint [1–5]. The applications and uses of polymer–surfactant systems are numerous, i.e. rheology control, solubilization, separation, control of surfactant mildness, drug-delivery, surface conditioning, etc. [2]. Many experimental approaches have been used to study polymer–surfactant interactions such as turbiditimetry [6, 7], light scattering [8, 9], small-angle neutron scattering [10], dialysis [11], surface tension [12–14], viscometry [9, 12], and calorimetry [15] etc. Most of the experimental studies on polymer–surfactant interactions in recent years have dealt with interactions between polyelectrolytes and oppositely charged surfactant monomers [16–19]. Spectroscopic techniques have also become successful in investigating phenomenon that occurs in polyelectrolyte-surfactant systems [20–23]. All investigations indicated that at low additions of surfactants to a dilute polyelectrolyte solution a cooperative binding of surfactant sets in above a concentration, which is lower than the ordinary critical micellization concentration (cmc) of the pure surfactant. The polyelectrolyte eventually becomes saturated with surfactant molecules, and free micelles appear in the system.

The strong association between oppositely charged surfactant and polyelectrolytes was attributed to the mutual action of electrostatic and hydrophobic forces between surfactant ions and polyelectrolytes, and between the hydrocarbon chains of bound surfactant ions, respectively. Winnik et al. [24] studied the interactions of pyrene-labeled hydroxypropyl cellulose (PyHPC) and PEO (PyPEO) [25] with sodium dodecyl sulfate (SDS). Both excimer/monomer emission intensity ratio (I_E/I_M) and I_3/I_1 indicated that these polymers associate with surfactants and form polymer surfactant micelles below the cmc. Hansson et al. [26] have investigated the interactions of alkyltrimethylammonium bromide (C_nTAB) with sodium carboxy methyl cellulose (CMC) in dilute solutions. The effect of salt on the binding to CMC of high linear charge density was investigated using a surfactant sensitive electrode and compared with the behavior in other polyelectrolyte systems. Taylor et al. [27] have studied the interactions between the oppositely charged surfactant/polymer mixtures using neutron reflectometry with supplementary surface tension measurements. They observed that in the presence of added electrolyte, the air/water surface of solutions of poly (styrene sulfonate). (PSS)/DTAB and PVPmCl/SDS, consists of a thin adsorbed film at low surfactant concentration and changes to a layered and thin structure at higher concentrations of surfactant up to and beyond the normal cmc. Recently, Yoshimura et al. [28] have studied the interactions of DTAB, 10-2-10, and 12-2-12 cationic surfactants with PSS and demonstrated the presence of both electrostatic as well as hydrophobic interactions between them.

In view of all these studies, in continuation of our previous work [29], there is very little known regarding the comparative interactions between a series of monomeric and dimeric cationic surfactants with anionic polyelectrolytes. The present work consists of a comprehensive fluorescence study of such cationic surfactants with anionic polyelectrolytes such as CMC, dextran sulfate (DX), PSS, and polyacrylic acid (PAA). The results have been evaluated on the basis of both head group as well as hydrophobic tail modifications in a series of cationic surfactants.

Experimental section

Materials

DTAB, TTAB, and HTAB from Lancaster Synthesis, UK, were used as received. 10-2-10 and 12-2-12 were synthesized as reported in the literature [30]. CMC (average molecular weight 100,000), DX (average molecular weight 500,000), PSS (average molecular weight 70,000), and PAA (average molecular weight 30,000) were obtained from TCI, Japan, and used without purification. Pyrene from Aldrich and quencher, hexadecylpyridinium chloride (HPyCl) from Lancaster Synthesis, UK, were used as received. Water was purified by deionization followed by double distillation. The solutions were prepared on the basis of their mass with an accuracy of 0.01 mg. All measurements have been performed at 25 °C after giving sufficient time for stabilization.

Method

Fluorescence measurements

Steady-state fluorescence spectra of pyrene in the mixed systems were obtained by using a Hitachi F-2500 fluorescence spectrophotometer at 25 °C in the range 350–500 nm. Fluorescence emission spectra of these solutions were recorded employing an excitation wavelength of 334 nm, and the intensities I_1 and I_3 were measured at the wavelengths corresponding to the first and third vibronic bands located at ca. 373 and 384 nm. The pyrene concentration was around 10^{-6} mol dm^{-3}. The errors in cmc values were estimated to be less than 10%. The mean aggregation number (N_{agg}) and micropolarity of various mixed systems were determined by using HPyCl under steady state conditions. It is being considered that the time of the quencher in micelle remains longer than the fluorescence lifetime of the probe. A suitable [pyrene]/[micelle] and [quencher]/[micelle] ratio ensures the Poisson distribution. The quenching of fluorescence of pyrene by HPyCl has been utilized to find out N_{agg}[31, 32]. The relevant relationship is given by

$$\ln\left(I_o/I_1\right) = \frac{[\mathrm{Quencher}]\, N_{\mathrm{agg}}}{[\mathrm{Surf}] - \mathrm{cmc}}, \qquad (1)$$

where I_o and I_1 are the fluorescence intensities in the absence and presence of quencher, respectively, and [Surf] is the total surfactant concentration, which was always kept at least five times the cmc.

Results

An appropriate fluorescence probe-like pyrene can be used to evaluate the microenvironment in which the probe resides. For a typical oppositely charged polyelectrolyte-surfactant system, pyrene is still a suitable hydrophobic probe in the sense that it can be solubilized easily in the nonpolar environment generated upon neutralization of the opposite polarities. Figure 1 demonstrates a typical micelle formation process in

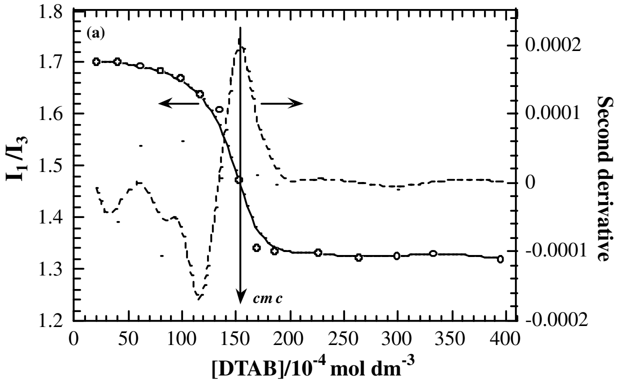

Fig. 1 Variation of the pyrene intensity, I_1/I_3 ratios with the total concentration of DTAB at 25 °C; (O) experimental points; the solid line represents the best sigmoidal fit to the experimental data; the dashed line corresponds to the second derivative of the sigmoidal curve; the vertical arrow denotes the cmc value

which the I_1/I_3 ratio of the pyrene intensity decreases as the micelle formation sets in. The cmc can be obtained from the second derivative of this plot. However, in the presence of oppositely charged anionic polyelectrolyte such as CMC, the typical micelle formation plot takes another shape, where two-step decrease in the I_1/I_3 ratio can be clearly observed as depicted in Fig. 2 for various surfactants. Similar plots were obtained for other surfactants in various present polyelectrolytes (not shown). The initial instantaneous decrease of I_1/I_3 value at T_1 indicates the onset of surfactant–polymer aggregation process traced by the continuous solubilization of pyrene in the aggregates and which ends at T_2. At T_2 whole of the surfactant is presumed to be complexed with the polyelectrolyte. Therefore, T_2 is the polymer saturation point or critical aggregation concentration (cac) of the complex formation between the monomeric cationic surfactant and polyelectrolyte. Therefore, a difference in the concentrations, i.e. T_2-T_1 should correspond to the amount of surfactant complexed with polyelectrolyte ($[\mathrm{Surf}]_{\mathrm{comp}}$). Beyond T_2, again I_1/I_3 starts decreasing with the increase in surfactant concentration till the arrival of T_3 and after this I_1/I_3 ratio becomes constant. A decrease in the I_1/I_3 beyond T_2 indicates the onset of independent micelle formation, which completes at T_3. Therefore, T_3 can be equated with the cmc of a surfactant in aqueous polyelectrolyte. These values have been listed in Table 1 for different surfactants in the presence of different amounts of aqueous anionic polyelectrolytes. Table 1 shows that for a particular surfactant, the T_1 and T_2 values show a little variation from one polyelectrolyte to another as well as with respect to a change in their amounts. Therefore, the value of ($[\mathrm{Surf}]_{\mathrm{comp}}$) also remains mainly quite close to each other for a particular surfactant in the presence of different polyelectrolytes. It is possible to calculate the degree of binding (β) between the oppositely charged cationic surfactants and anionic polyelectrolytes by applying the following equation:

$$\beta = \frac{[\mathrm{Surf}]_{\mathrm{comp}}}{[\mathrm{P_m}]}, \tag{2}$$

where $[\mathrm{P_m}]$ is the monomolar concentration of a polyelectrolyte. The β values thus calculated for various surfactants have also been listed in the second last column of Table 1. For a particular surfactant, the β value varies over a wide range, which can be clearly differentiated from that of other surfactants. One can see that there is a clear increasing trend in the β values with the decrease in hydrophobicity from HTAB to DTAB for monomeric cationic surfactants. It means that the degree of binding is maximum for DTAB + polyelectrolyte systems while minimum for HTAB + polyelectrolytes. Similar trend exists for dimeric + polyelectrolyte systems, where the values for 10-2-10 + polyelectrolyte systems are higher than that of 12-2-12 + polyelectrolytes.

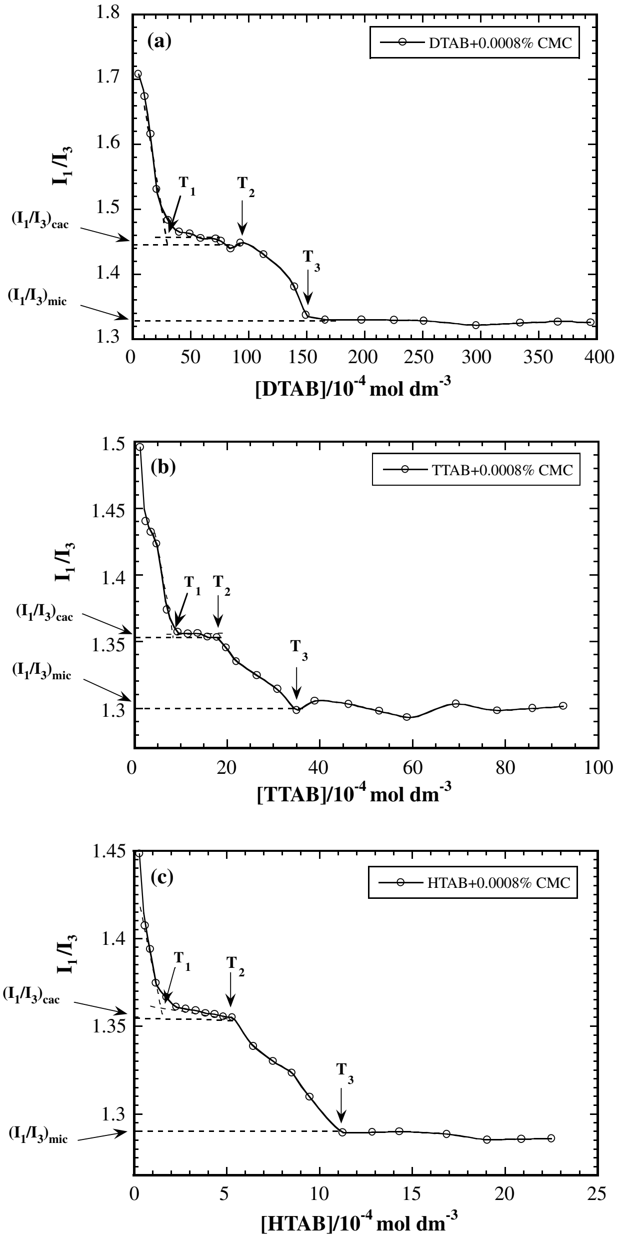

Fig. 2 **a** Variation of the pyrene intensity, I_1/I_3 ratios with the total concentration of DTAB in the presence of 0.0008% CMC. **b** Variation of the pyrene intensity, I_1/I_3 ratios with the total concentration of TTAB in the presence of 0.0008% CMC. **c** Variation of the pyrene intensity, I_1/I_3 ratios with the total concentration of HTAB in the presence of 0.0008% CMC

Micropolarity and mean aggregation number

As I_1/I_3 value indicates the micropolarity of the medium in which pyrene dissolves, therefore, such values for the

Table 1 Values of $T_1/10^{-4}$ mol dm^{-3}, $T_2/10^{-4}$ mol dm^{-3}, [Surf]$_{\mathrm{comp}}/10^{-4}$ mol dm^{-3}, $T_3/10^{-4}$ mol dm^{-3}, β, and N_{agg} for various surfactants from fluorescence measurements in the presence of polyelectrolytes

[Polyelectrolyte]	T_1	T_2 (cac)	[Surf]$_{\mathrm{comp}}$	T_3(cmc)	β	N_{agg}
HTAB + Polyelectrolytes						
Water				10		60 ± 3
0.0002% CMC						44 ± 2
0.0008% CMC	2.1	5.1	3.0	11	12	
0.0002% DX	2.1	4.5	2.4	14	19	47 ± 2
0.0004% DX	2.1	5.1	3.0	13	12	
0.0002% PSS	2.5	5.0	2.5	10	26	42 ± 2
0.0004% PSS	2.7	5.2	2.5	11	13	
0.0002% PAA	2.0	5.1	3.1	10	15	51 ± 3
TTAB + Polyelectrolytes						
Water				38		54 ± 3
0.0002% CMC	8.0	18.0	10.0	36	161	36 ± 2
0.0002% DX	7.0	20.0	13.0	53	106	52 ± 3
0.0002% PSS	8.0	22.0	14.0	40	144	36 ± 2
0.0002% PAA	7.2	13.9	6.7	40	32	63 ± 3
DTAB + Polyelectrolytes						
Water				152		48 ± 2
0.0002% CMC						33 ± 2
0.0004% CMC	30.0	90.0	60.0	158	484	
0.0008% CMC	30.0	95.0	65.0	150	262	
0.0002% DX	20.0	85.0	65.0	150	528	43 ± 2
0.0002% PSS	40.0	85.0	45.0	154	464	30 ± 1
0.0004% PSS	40.0	90.0	50.0	160	258	
0.0002% PAA	45.0	90.0	45.0	150	212	47 ± 2
10-2-10 + Polyelectrolytes						
Water					65	23 ± 1
0.0002% CMC						15 ± 1
0.0008% CMC	16.0	38.0	22.0	62	89	
0.0002% DX	12.0	25.0	13.0	46	105	31 ± 2
0.0004% DX	14.0	28.0	14.0	62	57	
0.0002% PSS	12.0	27.0	15.0	61	155	17 ± 2
0.0004% PSS	12.0	30.0	18.0	65	93	
0.0002% PAA	17.0	40.0	23.0	61	108	24 ± 1
12-2-12 + Polyelectrolytes						
Water					9	21 ± 1
0.0002% CMC						9 ± 1
0.0008% CMC	2.1	5.2	3.1	9	12	
0.0002% DX						19 ± 1
0.0008% DX	2.1	5.2	3.1	9	6	
0.0002% PSS						13 ± 1
0.0004% PSS	1.8	4.8	3.0	9	15	
0.0008% PSS	1.9	4.9	3.0	9	8	
0.0002% PAA	3.2	5.2	2.0	11	9	16 ± 1

surfactant–polymer aggregates available at the cac, $(I_1/I_3)_{\mathrm{cac}}$, and the cmc, $(I_1/I_3)_{\mathrm{mic}}$, has been evaluated as shown in Fig. 2. Both $(I_1/I_3)_{\mathrm{cac}}$ and $(I_1/I_3)_{\mathrm{mic}}$ have been plotted in Figs. 3 and 4, respectively, against the number of carbon atoms present in surfactant tail (n_c). The $(I_1/I_3)_{\mathrm{cac}}$ value (Fig. 3) for monomeric cationic surfactant + polyelectrolyte complexes decreases with the increase in n_c and it is maximum in the presence of PAA while minimum in the presence of DX. However, this difference is not very clear for $(I_1/I_3)_{\mathrm{cac}}$ in the case of dimeric cationic surfactants, though the fall in the values is much stronger (Fig. 3). On the other hand, the $(I_1/I_3)_{\mathrm{mic}}$ value (Fig. 4) for monomeric surfactants show a small decrease with the increase in n_c and they are not very much different from each other in the presence of various polyelectrolytes. The results of both figures suggest that the cationic monomeric surfactant + PAA complex is least while that of cationic monomeric surfactant + DX is maximum hydrophobic among all the present polyelectrolytes. However, this difference is not clearly visible for the micellar aggregates (Fig. 4) in the presence of aqueous polyelectrolytes. The results are further evaluated by computing the N_{agg} by using Eq. 1.

Table 1 also lists the N_{agg} value of various surfactants in the absence and presence of polyelectrolytes. A close inspection of Table 1 indicates that at a fixed amount of

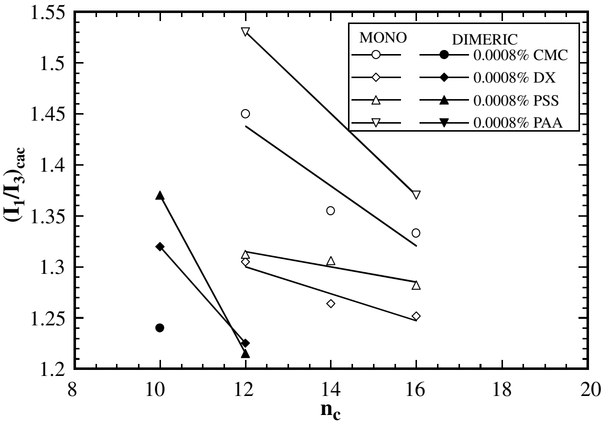

Fig. 3 Plot of $(I_1/I_3)_{cac}$, versus number of carbon atoms, n_c for monomeric and dimeric cationic surfactants at 0.0008% polyelectrolyte concentration

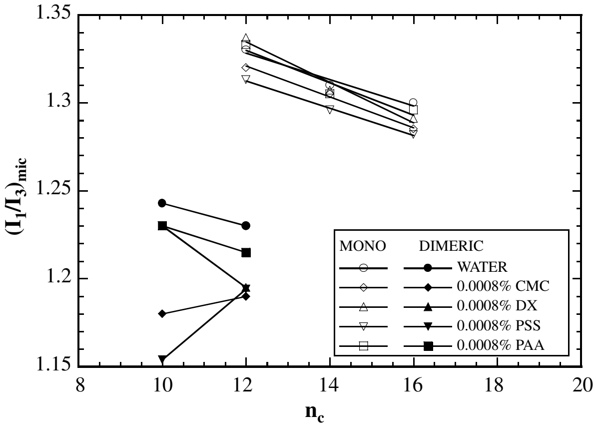

Fig. 4 Plot of $(I_1/I_3)_{mic}$, versus number of carbon atoms, n_c for monomeric and dimeric cationic surfactants at 0.0008% polyelectrolyte concentration

each polyelectrolyte, the N_{agg} value of each surfactant is mostly higher in the presence of PAA among all the polyelectrolytes and it is most of the time closer to that in pure water. The N_{agg} value in the presence of PSS is mostly minimum among all the polyelectrolytes, which can be attributed to the hydrophobic character of repeating aromatic groups that reduce the cooperative binding with oppositely charged cationic surfactants [33].

Discussion

The present study clearly indicates the presence of the conventional three-step process of surfactant–polyelectrolyte interactions involving both cac as well as cmc. However, no cooperative binding has been seen which may be due to a very low concentration of the polyelectrolytes involved in order to avoid the insoluble salt formation particularly for the fluorescence studies. A decrease in β with the increase in hydrophobicity of a cationic surfactant can obviously be related to the screening of electrostatic interactions due to the folding of long hydrophobic tail and which may not be so effective in the case of a surfactant with a short hydrophobic tail. Among the present polyelectrolytes, the surfactant–PAA complex induces higher N_{agg} value, while surfactant–PSS complex results in lowest N_{agg} values. The latter has already been reported [33] on the basis of the hydrophobic nature of repeating aromatic units reducing the cooperative binding while the former can be due to the cooperative binding which is of course not very clear from Table 1. On the other hand, Fig. 3 demonstrates that the micropolarity of the aggregates at the cac is maximum for PAA and minimum for DX, while this difference does not exist in the micropolarity of the micellized surfactants (Fig. 4). It means that the difference in micropolarities shown in Fig. 3 should infact indicate the difference in the hydrophobic environment of the aggregates. The surfactant—PAA aggregates having least hydrophobic environment among all the polyelectrolytes since large numbers of surfactant monomers have been associated cooperatively with PAA thus providing micellar arrangement with higher N_{agg}. At high surfactant concentration where a clear difference in the micropolarity vanishes (Fig. 4) can be attributed to the solubilization of each surfactant–polyelectrolyte complex in the micellar phase.

Conclusions

The following conclusions can be drawn from this study.

1. A typical three-step oppositely charged surfactant–polyelectrolyte process involving cac and cmc has been observed for all systems.
2. The degree of binding of cationic surfactants with polyelectrolytes decreases with the increase in length of the hydrophobic tail.
3. Among all the polyelectrolytes, PAA induces higher N_{agg} and higher micropolarity at the cac.

Acknowledgements Financial assistance from CSIR under a research project (Ref. No. 01(1777)/02/EMR-II) is thankfully acknowledged.

References

1. Goddard ED (1986) Colloids Surf 19:301
2. Goddard ED, Ananthapadmanabhan KP (1993) Interactions of surfactants with polymers and proteins. CRC Press, Boca Raton
3. Hayakawa K, Kwak JCT (1991) Cationic surfactants. In: Rubingh DN, Holland PM (eds) Physical chemistry. Marcel Dekker, New York, p 189
4. Fundin J, Brown W, Vethamuthu MS (1996) Macromolecules 29:1195
5. Thalberg K, Lindman B (1993) Colloids Surf A Physicochem Eng Asp 76: 283
6. Dubin PL, Rigsbee DR, McQuigg DW (1985) J Colloid Interface Sci 105:509
7. Dubin PL, Oteri RJ (1983) Colloid Interface Sci 95:453
8. Xia J, Dubin PL, Kim Y (1992) J Phys Chem 96:6805
9. Li Y, Xia J, Dubin PL (1994) Macromolecules 27:7049
10. Cabane B, Duplessix R (1982) J Phys (Paris) 43:1529
11. Shirahama K (1974) Colloid Polymer Sci 252:978
12. Jones MN (1967) J Colloid Interface Sci 23:36
13. Schwuger MJ (1973) J Colloid Interface Sci 43:491
14. Murata M, Arai H (1973) J Colloid Interface Sci 44:475
15. Rigsbee DR, Dubin PL (1996) Langmuir 12:1928
16. Wei YC, Hudson JM (1995) J Macromol Sci C 35:1
17. Hayakawa K, Santerre JP, Kwak JCT (1983) Macromolecules 16:1642
18. Malovikova A, Hayakawa K, Kwak JCT (1984) J Phys Chem 88:1930
19. Bergeron V, Langevin D, Asnacios A (1996) Langmuir 12:1550
20. Abuin EB, Scaiano JC (1984) J Am Chem Soc 106:6274
21. Chu D, Thomas JK (1986) J Am Chem Soc 108:6270
22. Gao Z, Kwak JCT, Wasylishen RE (1988) J Colloid Interface Sci 126(1): 371
23. Almgren M, Hansson P, Mukhtar E, van Stam J (1992) Langmuir 8:2405
24. Winnik FM, Winnik MA, Tazuke S (1987) J Phys Chem 91:594
25. Hu Y, Zhao C, Winnik MA (1990) Langmuir 6:880
26. Hansson P, Almgren M (1996) J Phys Chem 100:9038
27. Taylor DJF, Thomas RK, Hines JD, Humphreys K, Penfold J (2002) Langmuir 18:9783
28. Yoshimura T, Nagata Y, Esumi K (2004) J Colloid Interface Sci (in press)
29. Bakshi MS, Sachar S (2004) Colloid Polymer Sci 282:993
30. Zana R, Benrraou M, Rueff R (1991) Langmuir 7:1072
31. Turro NJ, Gratzel M, Braun AM (1980) Angew Chem Int Ed Engl 19:675
32. Malliaris A (1987) Progr Colloid Polym Sci 73:161
33. Hayakawa K, Kwak JCT (1982) J Phys Chem 86:3866