Colloid Polym Sci 275:850–859 (1997)

ORIGINAL CONTRIBUTION

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Micellization of cetyltrimethylammonium bromide in the presence of 9-anthryl alkanols

Received: 26 March 1997
Accepted: 16 May 1997

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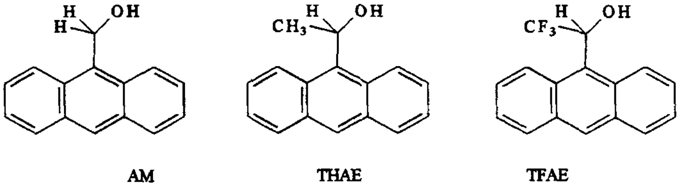
Abstract Surface tension measurements in aqueous cetyltrimethyl ammonium bromide were performed in presence of various amounts of 9-(hydroxymethyl)anthracene (AM), 9-[1-(1-hydroxy)ethyl]anthracene (THAE), and 9-[1-(1-hydroxy-2,2,2-trifluoro)ethyl]anthracene (TFAE). Free energies $\Delta G_m^\ominus$ and $\Delta G_i^\ominus$ of micellization and of adsorption to the air–water interface, respectively, were determined as well as the corresponding enthalpies and entropies. $\Delta G_m^\ominus$ of micellization increased in the presence of AM and THAE, but became more negative when TFAE was added. In contrast to AM and THAE, TFAE addition decreases $\Delta S_i^\ominus$. For this peculiarity of TFAE, its location and orientation in micellar solution was investigated by means of UV and ^{19}F-NMR spectroscopy.

Key words Surfactants – micellization – solubilization

Introduction

The influence of certain anthracene derivatives and their photoreactions on the flow behavior of aqueous cetyltrimethylammonium bromide (CTAB) has been subject of several rheological and light-scattering studies, which have been reviewed recently [1, 2]. Macroscopically, light-induced changes of viscosity and flow properties were observed originating from effects that the anthracene derivatives and their photodimers had on size and shape of micellar aggregates as well as on micellar hydration shells [3–6]. Our interest in the origins of these phenomena prompted us to study the micellization process of CTAB in the presence of the following three anthryl alkanols 9-hydroxymethylanthracene (= 9-anthrylmethanol, AM), 9-(1-(1-hydroxy)ethyl)anthracene (THAE), and 9-(1-(1-hydroxy-2,2,2-trifluoro)ethyl)anthracene (= 2,2,2-trifluoro-1-(9-anthryl)ethanol, TFAE) (Scheme 1).

The former two solubilizates are known to increase bulk viscosities of aqueous micellar CTAB solutions (due to the formation of big globular micelles) while the latter additionally induces viscoelastic behavior (due to the formation of long thread-like micelles) [5–7]. In this case, therefore, the investigations were completed by UV-absorption studies designed to explore the immediate vicinity of TFAE solubilized at CTAB concentrations around the critical micelle concentration, and by ^{19}F-NMR-spectroscopic measurements.



Scheme 1

Experimental

Materials

Cetyltrimethylammonium bromide (Merck, p.a.) was recrystallized three times from acetone-methanol (9:1

mixture). 9-(Hydroxymethyl)anthracene (Aldrich, 97%) was chromatographed on basic alumina and recrystallized from ethanol. 9-(1-(1-Hydroxy-2,2,2-trifluoro)ethyl)anthracene (Aldrich, racemic mixture, 98%) was used as supplied. 9-(1-(1-Hydroxy)ethyl)anthracene was prepared following a literature procedure [8].

Sample preparation

Micellar solutions were prepared using triply distilled water that was passed through 50 nm filters. After weighing in water and the desired chemicals the solubilization was accelerated by heating the sealed samples to 60 °C and periodically exposing them to an ultrasonic bath. All solutions had to be stored in the dark (in order to avoid photodimerization of anthracenes [1–5]) and were measured within 48 h after preparation.

Surface tension measurements and evaluation of surface tension data

A Krüss model T8600 tensiometer was used to measure surface tensions employing the ring method (ring diameter 2.5 cm). The solutions kept at the desired temperature (in the dark) were measured 30 s after transfer to the thermostatted measuring dishes. The actual temperature within the dishes was controlled prior to and after the measurement by means of thermocouple. Deviations from the desired temperature were ±0.2 K at temperatures below and ±0.5 K above 45 °C. The values of cmc were determined from plots of surface tension vs the logarithm of the CTAB concentration revealing two regions of differing slope resembled by straight lines which intersect at the cmc [9]. Examples for original surface tension values as a function of concentration are given in Ref. [10]. Thermodynamic parameters of micellization (free energy, enthalpy and entropy) were determined using the equations

$$\Delta G_{\mathrm{m}}^{\ominus} = RT \ln X_{\mathrm{cmc}} , \tag{1}$$

$$\Delta H_{\mathrm{m}}^{\ominus} = -RT^2 (\partial \ln X_{\mathrm{cmc}}/\partial T)_p , \tag{2}$$

$$\Delta S_{\mathrm{m}}^{\ominus} = [(\Delta G_{\mathrm{m}}^{\ominus} - \Delta H_{\mathrm{m}}^{\ominus})/T]_p , \tag{3}$$

where X_{cmc} is the molar fraction of surfactant at cmc. R, T, p are gas constant, temperature and pressure, respectively. One should be aware that determinations according to Eqs. (1–3) rest on the validity of the "pseudo phase model" [11, 12], problems in that respect are discussed in detail by Fisher and Oakenful [13] as well as by Blandamer et al. [14]. The model proved applicable for surfactants bearing hydrocarbon chains exceeding 10 C-atoms [15–18] like CTAB.

Thermodynamic parameters for the process of surfactant adsorption to the air–water interface were determined from the slopes of plots of surface tension (σ) vs $\log c_{\mathrm{s}}/c^{\ominus}$ (c_{s} = volume concentration of surfactant) [19]. The free energy $\Delta G_{\mathrm{i}}^{\ominus}$ of adsorption of CTAB at the air–water interface was determined at various temperatures from Eq. (4), the corresponding enthalpy change $\Delta H_{\mathrm{i}}^{\ominus}$ then was calculated from Eq. (5) and $\Delta S_{\mathrm{i}}^{\ominus}$ analogously to Eq. (3):

$$\Delta G_{\mathrm{i}}^{\ominus} = -RT \ln[(c_{\mathrm{s}}/c^{\ominus})/(c'_{\mathrm{s}}/c'^{\ominus}_{\mathrm{s}})] , \tag{4}$$

$$\Delta H_{\mathrm{i}}^{\ominus} = \Delta G_{\mathrm{i}}^{\ominus} - T[\delta(\Delta G_{\mathrm{i}}^{\ominus})/\delta T] . \tag{5}$$

Here c'_{s} is the lateral surfactant concentration at the interface, which is also used to calculate the area per surfactant head group A_{s} and the actual interfacial concentration c_{i} (in good approximation [20]) from Eq. (6)

$$A_{\mathrm{s}} = 1/c_{\mathrm{i}} = 1/(c_{\mathrm{e}} + c'_{\mathrm{s}}) . \tag{6}$$

For strongly surface active substances $c_{\mathrm{i}} \simeq c_{\mathrm{e}}$. In aqueous CTAB around cmc the approximation $c_{\mathrm{i}} = c_{\mathrm{e}}$ constitutes an error of $<0.5\%$ [20]. In most of the calculations in the literature this approximation is not mentioned (cf. Ref. [19, 21, 22]). To determine A_{s} we obtain c_{e}, the excess concentration of surfactant molecules at the interface, with the help of Eq. (7)

$$c_{\mathrm{e}} = -(2.303\,RTk)^{-1}[\mathrm{d}\sigma/\mathrm{d}\log(c_{\mathrm{s}}/c^{\ominus})] . \tag{7}$$

The value of the constant k in Eq. (6) is controversially discussed in the literature. Pethika [23] suggested $k = 2$ for diluted surfactant solutions without added electrolyte and $k = 1$ for concentrated solutions in the presence of electrolyte. Weil [20] determined $k = 1.7$ for various dodecylsulfates (without additional electrolyte), while Mankowich [19] found maximum coincidence of literature values for $k = 1$. In this study we adjusted $k = 1.6$ according to the best agreement of area-per-headgroup values for pure aqueous CTAB with literature data (ca. 45 Å² [24–26]). The value $k = 1.6$ also follows when dissociation of counterions is taken into account (leaving the pseudo phase model). Then

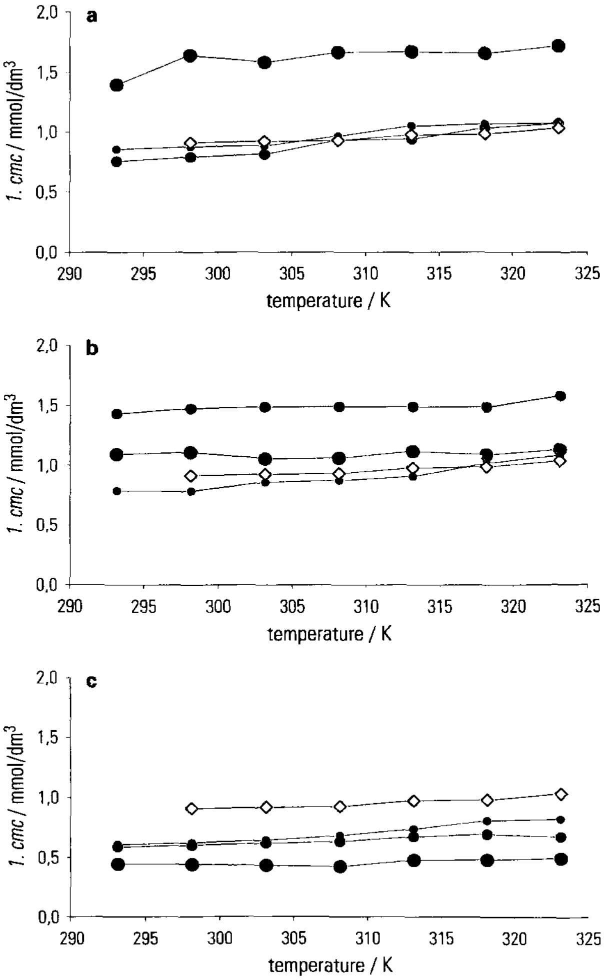
$$k = 1 + h , \tag{8}$$

where h is the fraction of counterions bound to the micelle. According to various studies h in CTAB ranges from 0.6 to 0.78 [27–29].

Spectra

Ultraviolet spectra were recorded using a Perkin Elmer Lambda 19 Spectrophotometer that was controlled through a DEC 486sx personal computer. It was verified that the measurement of the UV-spectra itself did not cause any appreciable photodimerization of the anthracenes: the absorption did not vary by more than 0.5% in consecutive measurements. ^{19}F-NMR-spectra were obtained with Bruker WH 400E spectrometer. Temperatures were recorded as given by the built in thermometers of the above spectrometer. ^{19}F-spectra were calibrated by means of a sealed capillary filled with hexafluorobenzene (simultaneously providing the necessary lock-in signal) within the actual probe as to avoid problems induced by contamination of micellar solutions with a deuterated solvent.

Fig. 1 Critical micelle formation concentrations (cmc) of CTAB as a function of temperature in the presence and absence of AM, THAE, and TFAE. a) (◇) pure CTAB; (•) CTAB:AM = 25:1; (•) CTAB:AM = 25:3; (●) CTAB:AM = 25:5. b) (◇) pure CTAB; (•) CTAB:THAE = 25:1; (•) CTAB:THAE = 25:3; (●) CTAB:THAE = 25:5. c) (◇) pure CTAB; (•) CTAB:TFAE = 25:1; (•) CTAB:TFAE = 25:3; (●) CTAB:TFAE = 25.5

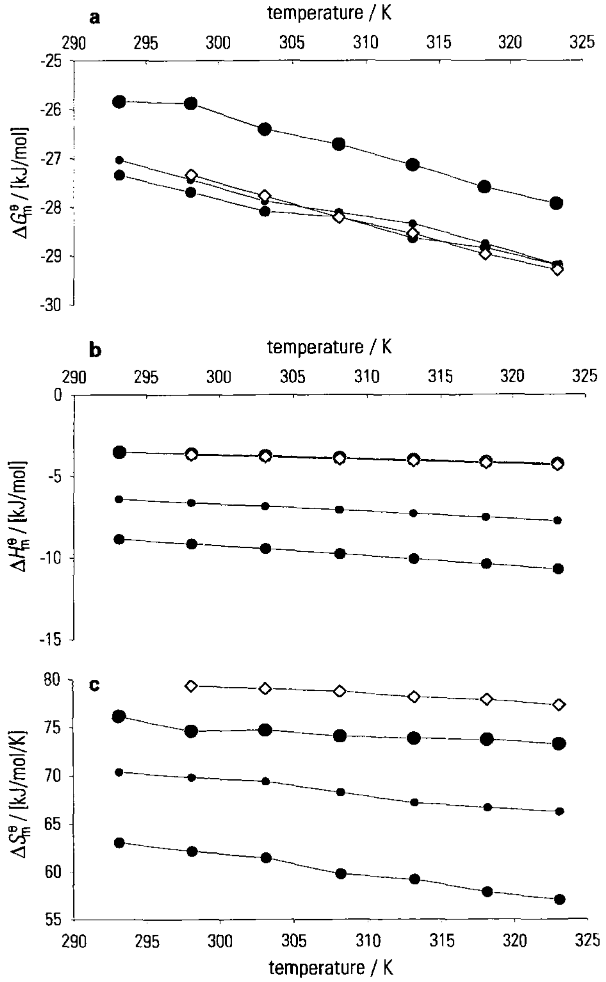


Results

Surface tension

Figure 1 displays values of the first critical micelle formation concentration, cmc, as a function of temperature for CTAB in the presence of AM, THAE, and TFAE. Inspection reveals that in AM and THAE at low solubilizate concentration (CTAB:AM = CTAB:THAE = 25:1) cmc values do not much deviate from pure aqueous CTAB. The same holds for CTAB:AM = 25:3, while at CTAB:AM = 25:5 cmc values are increased by a factor of 2. In THAE a doubled cmc is observed at the intermediate concentration ratio 25:3, whereas at 25:5 the values are close to the pure CTAB. TFAE behaves differently. The

Fig. 2 Thermodynamic parameters ΔG_m, ΔH_m, and ΔS_m for micelle formation (addition of CTAB monomers to micelles) as a function of temperature in the absence and presence of AM. (◇) pure CTAB; (•) CTAB:AM = 25:1; (•) CTAB:AM = 25:3; (●) CTAB:AM = 25:5



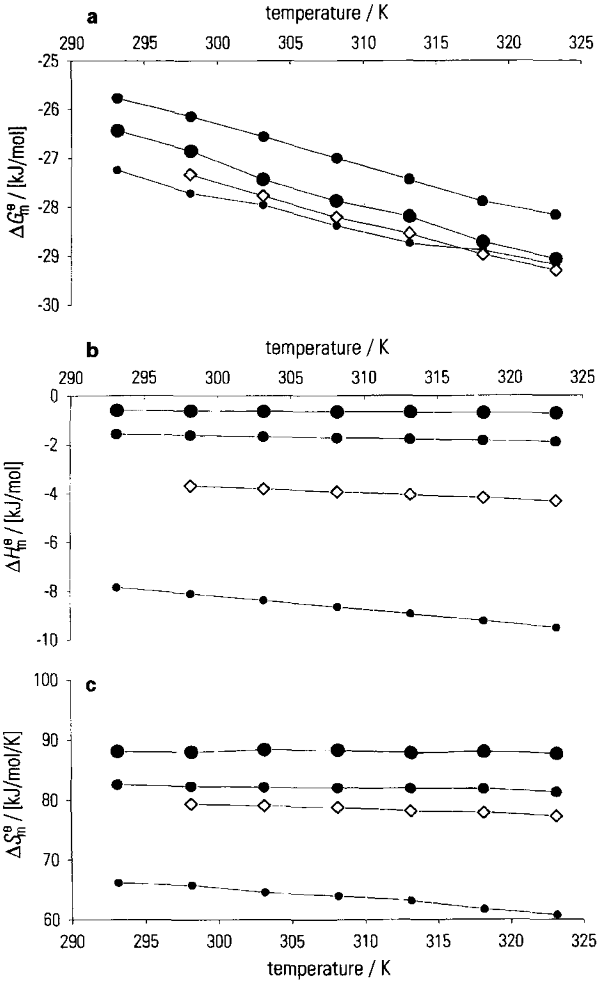


Fig. 3 Thermodynamic parameters ΔG_m, ΔH_m, and ΔS_m for the formation of micelles (addition of CTAB monomers to micelles) as a function of temperature in the absence and presence of THAE. (◇) pure CTAB; (•) CTAB:THAE = 25:1; (●) CTAB:THAE = 25:3; (●) CTAB:THAE = 25:5

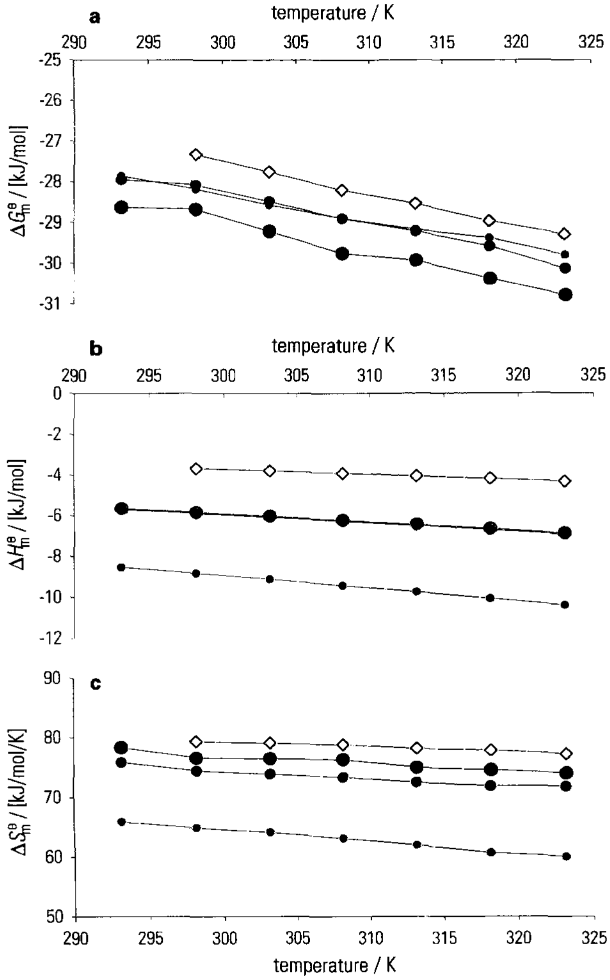


Fig. 4 Thermodynamic parameters ΔG_m, ΔH_m, and ΔS_m for the formation of micelles (addition of CTAB monomers to micelles) as a function of temperature in the absence and presence of TFAE. (◇) pure CTAB; (•) CTAB:TFAE = 25:1; (●) CTAB:TFAE = 25:3; (●) CTAB:TFAE = 25:5

cmc values decrease with increasing TFAE concentration down to one half of the value in pure aqueous CTAB.

The thermodynamic micellization parameters are comprised in Figs. 2–4. $\Delta G_m^\ominus$ values follow the tendencies described above for cmc values. At CTAB : AM = 25 : 5 the micelle formation thermodynamics almost agrees with that of the system without solubilizate. In the other systems certain specialities can be obtained when $\Delta H_m^\ominus$ and $\Delta S_m^\ominus$ are inspected. Two distinct trends can be found: (i) micellization is more exothermic but less entropically favored as compared to pure aqueous CTAB; this holds for the two lower CTAB:AM ratios, for CTAB:THAE = 25:1, and for all three CTAB:TFAE ratios. (ii) The exothermicity of micellization is strongly decreased but compensated by a rather big entropy of micellization; this was observed for the two higher CTAB:THAE ratios.

The areas per head group A_s determined using Eq. (6) are comprised in Fig. 5. In AM and THAE at low and medium solubilizate content there is not much difference in A_s as compared to CTAB without additive. At the 25:5 ratios, however, the area per head group increases probably due to incorporation of solubilizate molecules into the interface layer. In TFAE the area per head group is diminished at CTAB:TFAE = 25:1, while it is increased at the ratios of 25:3 and 25:5.

Figures 6–8 show thermodynamic parameters for the adsorption of CTAB molecules at the air–water interface. Here TFAE induces exactly opposite effects when

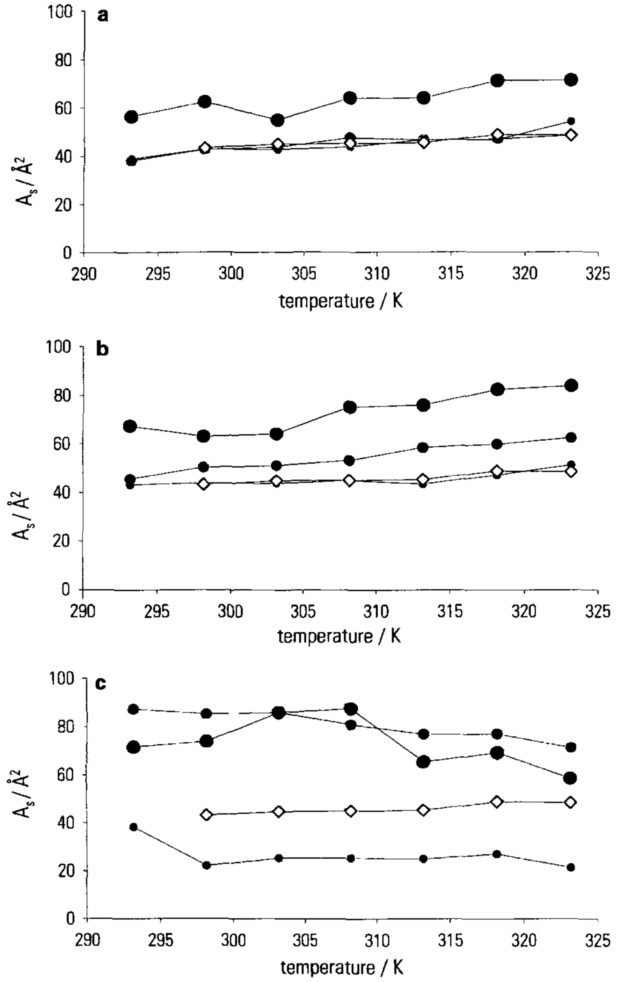


Fig. 5 Areas per head group A_s of CTAB at the air-water interface in the presence and absence of AM, THAE, and TFAE. (a) (◇) pure CTAB; (•) CTAB:AM = 25:1; (●) CTAB:AM = 25:3; (●) CTAB:AM = 25:5. (b) (◇) pure CTAB; (•) CTAB:THAE = 25:1; (●) CTAB:THAE = 25:3; (●) CTAB:THAE = 25:5. (c) (◇) pure CTAB; (•) CTAB:TFAE = 25:1; (●) CTAB:TFAE = 25:3; (●) CTAB:TFAE = 25:5

compared with AM and THAE in that it increases exothermicity and decreases ΔS_i (down to negative values).

UV absorption spectra

Ultraviolet spectra of TFAE in submicellar CTAB solution failed to provide any indication of submicellar species such as those found by Sato et al. in their investigation of sodium dodecylsulfate systems in the presence of certain dyes [30, 31]. Corresponding measurements were carried out over several orders of magnitude and with varying ratios of CTAB:TFAE.

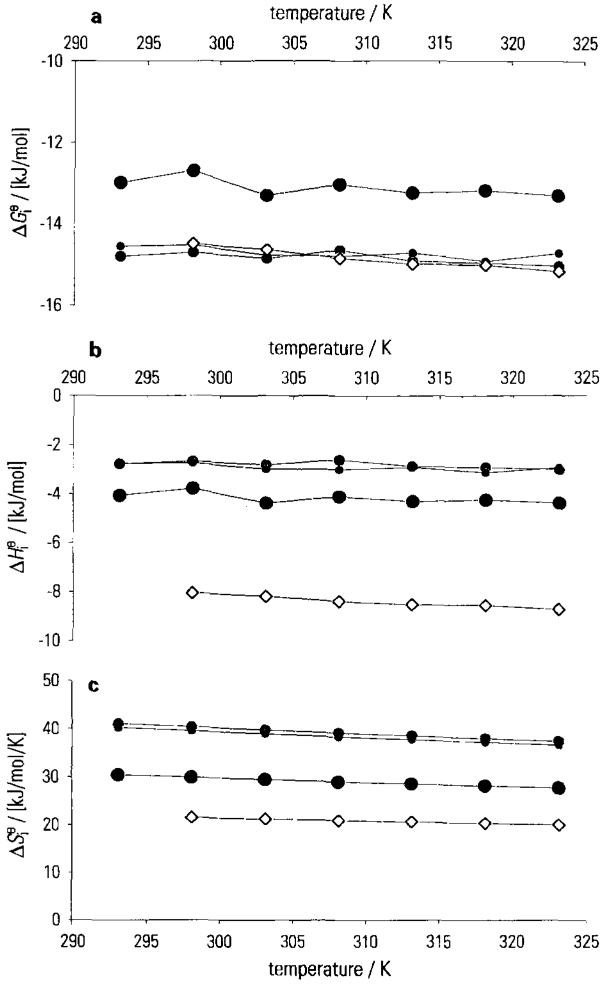


Fig. 6 Thermodynamic parameters ΔG_i, ΔH_i, and ΔS_i for the adsorption of CTAB monomers at the air–water interface as a function of temperature in the absence and presence of AM. (◇) pure CTAB; (•) CTAB:AM = 25:1; (●) CTAB:AM = 25:3; (●) CTAB:AM = 25:5

As shown in Fig. 9, the submicellar transition does not seem to leave significant marks on the UV spectra of the solubilizate. A 0.5 nm blue shift of the maximum is all there is to be observed across the transition from submicellar to micellar solutions, the same holds true for the corresponding CTAB:AM and CTAB:THAE solutions.

NMR spectra

^{19}F-NMR spectra of TFAE solutions were measured in more concentrated solutions usually containing between 30 and 50 mmol/dm^3 TFAE. This was necessary because of high proton content in aqueous micellar solutions and

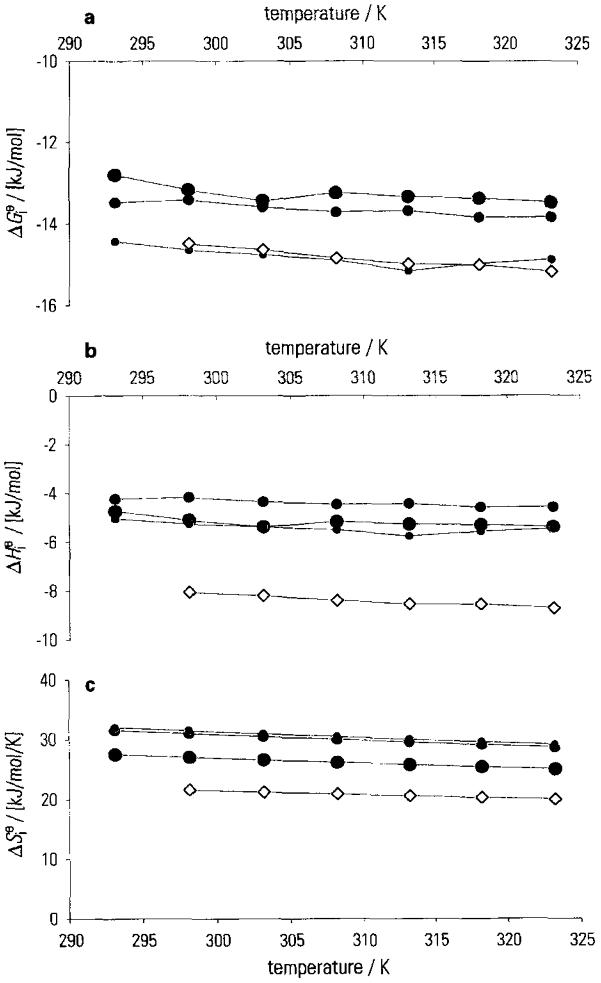


Fig. 7 Thermodynamic parameters ΔG_i, ΔH_i, and ΔS_i for the adsorption of CTAB monomers at the air–water interface as a function of temperature in the absence and presence of THAE. (◇) pure CTAB; (•) CTAB:AM = 25:1; (•) CTAB:AM = 25:3; (●) CTAB:THAE = 25:5

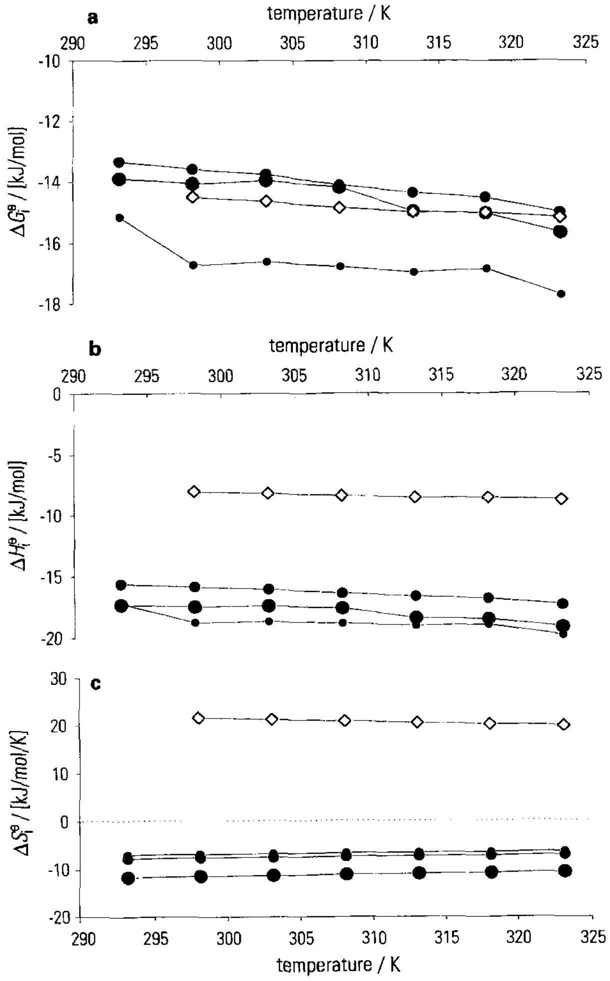


Fig. 8 Thermodynamic parameters ΔG_i, ΔH_i, and ΔS_i for the adsorption of CTAB monomers at the air–water interface as a function of temperature in the absence and presence of TFAE. (◇) pure CTAB; (•) CTAB:TFAE = 25:1; (•) CTAB:TFAE = 25:3; (●) CTAB:TFAE = 25:5

suboptimal lock-in-signal due to the use of an internal standard in a sealed capillary. However, the replacement of water by its fully deuterated equivalent would have rendered the results incomparable to the other experiments on standard aqueous solutions [32]. The high concentration lead to extremely viscous solutions at room temperature [1] and, consequently, massive line broadening further degrades signal quality (Fig. 10).

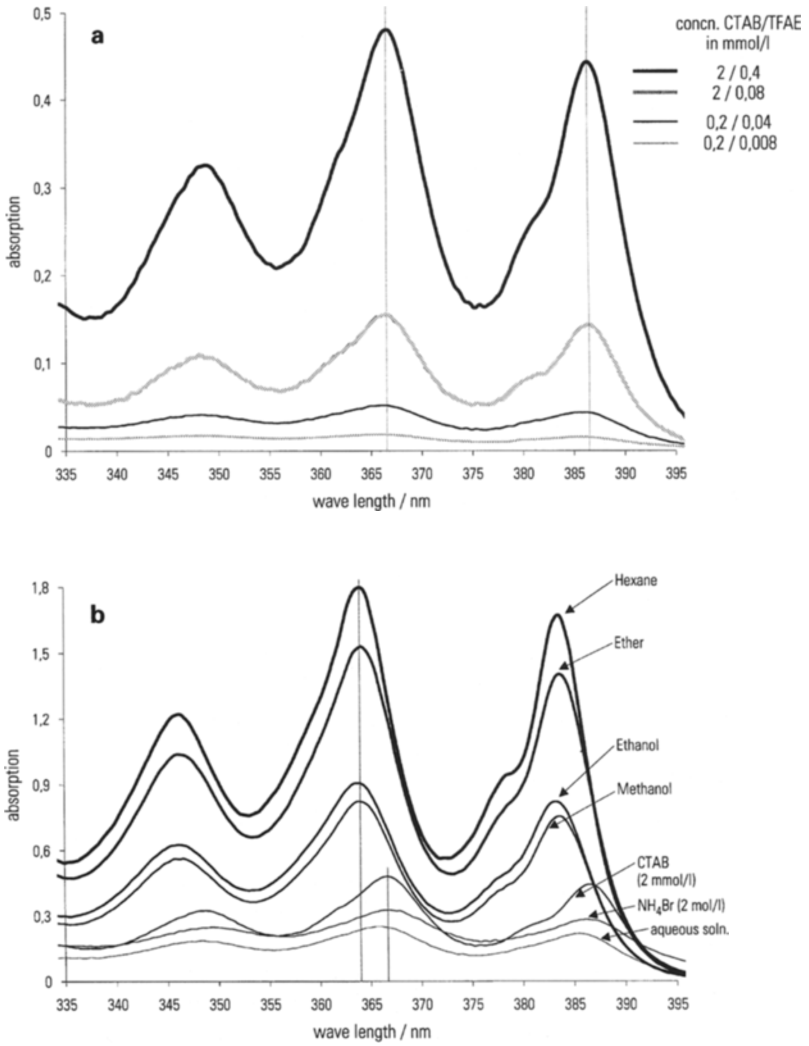
The viscosity of the micellar system in question is known to decrease with increasing temperature and increase in the ratio of CTAB:TFAE [5]. As expected this behavior is confirmed by the spectra shown in Fig. 10b. For comparison, the ^{19}F-signal of TFAE was recorded in various organic solvents – the results shown in Fig. 11 alongside the signal of TFAE in aqueous micellar CTAB solution. The latter signal is shifted considerably to lower field when compared with non-polar and medium-polar toluene and deuterochloroform solutions shown in Fig. 11. It is noteworthy that the ^{19}F-signal in polar organic solvents is shifted to high field, i.e., in the opposite direction.

Discussion

Thermodynamic micellization parameters

(1) CTAB-AM. Since influences of AM on cmc values appear at CTAB:AM = 25:5 only, we may conclude that

Fig. 9 UV absorption spectra of TFAE. (a) in aqueous CTAB at various CTAB concentrations and CTAB : TFAE ratios; (b) in various organic solvents



some amount of AM can be dissolved in the bulk water phase, perhaps mediated by complex formation of AM and a few CTAB monomers (premicellar aggregates, cf. Refs. [30, 31]). The formation of such premicellar aggregates may cause the slight increase in exothermicity observed at a lower solubilizate fractions. The micelles formed under these conditions should be similar to ordinary CTAB micelles, while at CTAB : AM = 25 : 5 a change of the aggregate takes place in order to incorporate more AM. The formation of premicellar aggregates vanishes at the 25 : 5 ratio as the enthalpy effect is no longer observed. Due to the lack of this enthalpy effect the formation of these modified micelle is energetically somewhat less favorable. This view is corroborated by the determinations of areas per CTAB head group which exhibit effects of AM at high solubilizate fractions only.

Generally, entropy is gained (up to 100% as compared to pure CTAB) in the process of CTAB adsorption at the air–water interface when AM is added. Since AM is not incorporated into the monolayer at low solubilizate fractions but affects the process, it can be expected to reside near the surface in the aqueous phase. Probably the complete premicellar aggregate mentioned above moves to the surface where entropically unfavorable interactions of AM and water are reduced.

(2) CTAB-THAE. A close similarity to the CTAB-AM system appears when one considers that effects showing up at CTAB : AM = 25 : 5 can be observed at the 25 : 3 ratio already when AM is exchanged by THAE.

(3) CTAB-TFAE. Here distinctions from the other two systems become obvious. Under all conditions investigated the cmc values are reduced as compared to pure CTAB. A modification of micellar aggregates already at low CTAB : TFAE ratios is likely. The increase in exothermicity of micelle formation is decisive for this effect since $\Delta S_{\mathrm{m}}^{\ominus}$ is decreased in the presence of TFAE. The further

variations of $\Delta H^\ominus_\mathrm{m}$ and $\Delta S^\ominus_\mathrm{m}$ with increasing TFAE fraction may point to a micellization mechanism agreeing with the other systems, with reduced cmc and $\Delta G^\ominus_\mathrm{m}$, however.

The area per head group also varies in a way differing from the systems containing AM and THAE. Most striking is the reduction of A_s at the lowest TFAE fraction to ca. 50% of the value in pure CTAB. This may be explained by a zig–zag ordering of monomers at the surface (every second monomer dipping deeper into the aqueous phase), induced by strong interactions with TFAE.

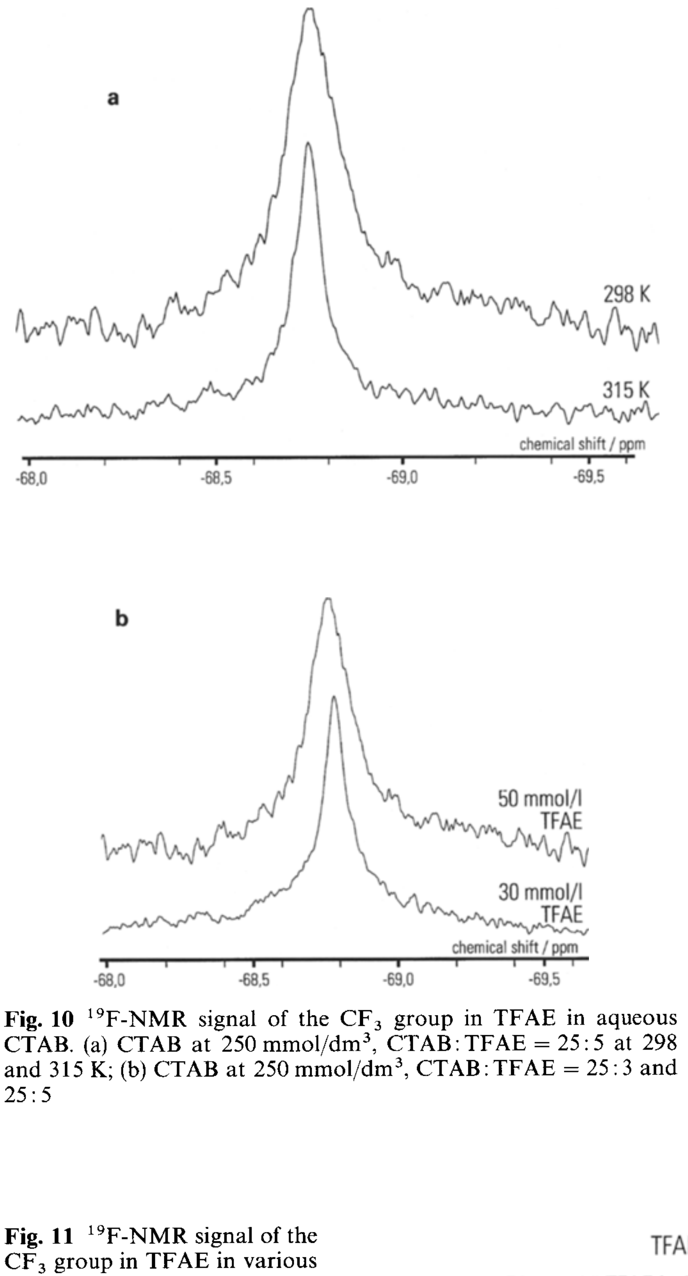
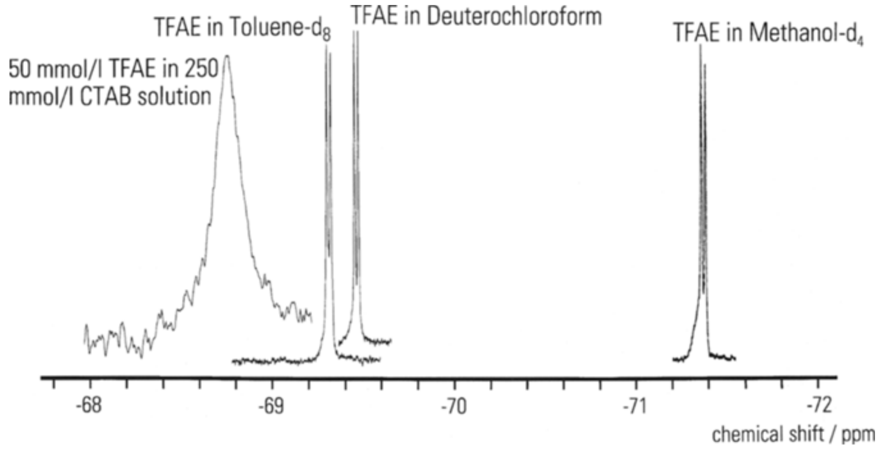


Fig. 10 ^{19}F-NMR signal of the CF_3 group in TFAE in aqueous CTAB. (a) CTAB at 250 mmol/dm^3, CTAB:TFAE = 25:5 at 298 and 315 K; (b) CTAB at 250 mmol/dm^3, CTAB:TFAE = 25:3 and 25:5

TFAE spectra

The distinctions of CTAB-AM and CTAB-THAE on one hand and the CTAB–TFAE system on the other are in keeping with the differing macroscopic flow behavior reported previously [5, 6]. Some deeper insight in the latter system arises from the spectroscopic experiments. The analysis of the spectroscopic results seems fairly straightforward if one considers UV and NMR spectra individually. From the UV spectra we may conclude that TFAE in micellar solution is situated in a predominantly aqueous environment. The position of the ^{19}F-NMR-signals of TFAE in various solvents and in aqueous micellar environments suggest that TFAE is located in an extremely "organic", non-polar region of the micellar solution. Both methods are accurate enough to allow us to deduce the molecular environment of TFAE from the respective data. The two methods give different, radically opposite results. They differ, however, also in the exact location of the probing part of the molecule. The UV absorption spectra measure the anthracene body while ^{19}F-signals obviously relate to the substituent. Unless the opposing results are a consequence of the higher concentration in the NMR

Fig. 11 ^{19}F-NMR signal of the CF_3 group in TFAE in various organic solvents



experiments, we may conclude that each method does provide accurate results for the part of the molecule it investigates. Hence, the molecule must be located in such a position that the polar CF_3-group is submitted to an unpolar environment while the anthracene body suffers aqueous ionic influence. In a micellar solution these conditions clearly constrain position and orientation of TFAE to the two possibilities shown in Fig. 12. It must be further realized that the clear difference in NMR and UV data require a rather fixed TFAE position in the micelles, i.e., the micellar aggregates in the presence of TFAE are less dynamic than ordinary CTAB micelles, with respect to motion inside the micelle, to shape and flexibility and to surfactant monomer exchange.

Acknowledgment This work is a project of the Graduiertenkolleg "Chemische Reaktivität und molekulare Ordnung" merituously financed by the Deutsche Forschungsgemeinschaft and by the Minister für Wissenschaft und Kunst des Landes Nordrhein-Westfalen. TW gratefully acknowledges financial support by the Fonds der Chemischen Industrie.

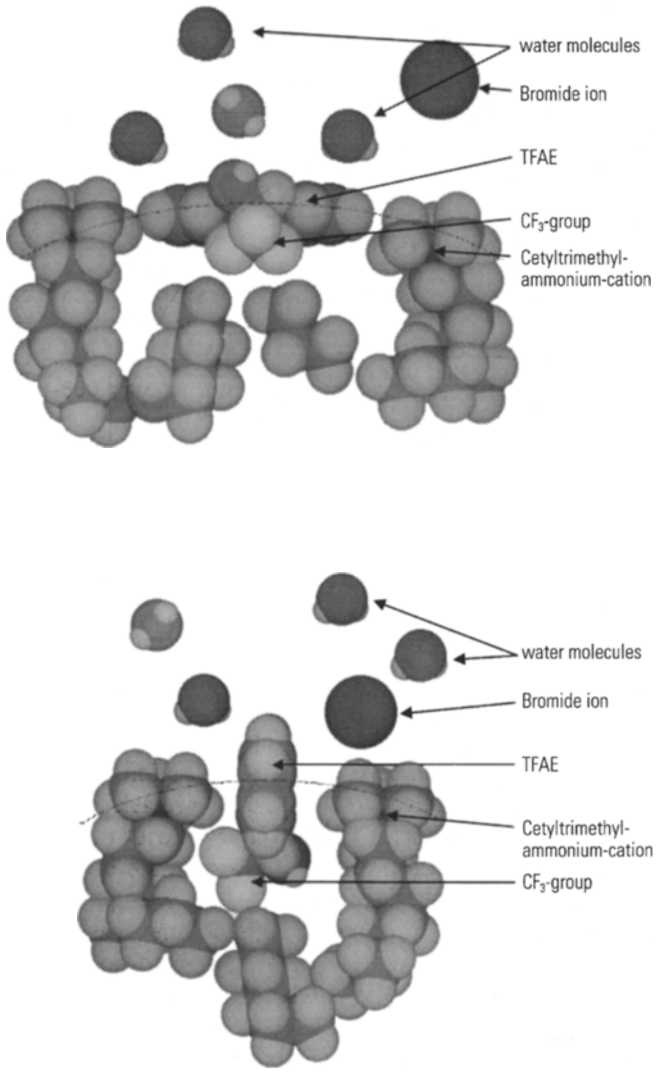


Fig. 12 Possible sites and orientations of TFAE in micellar environment

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