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Regioselectivity in the photodimerization of 9-hydroxy-methylanthracene and 9-anthracene carboxylic acid esters in surfactant systems

Andreas Schütz, Thomas Wolff *

Technische Universität Dresden, Institut für Physikalische Chemie und Elektrochemie, Mommsenstrasse 13, D-01062 Dresden, Germany

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Abstract

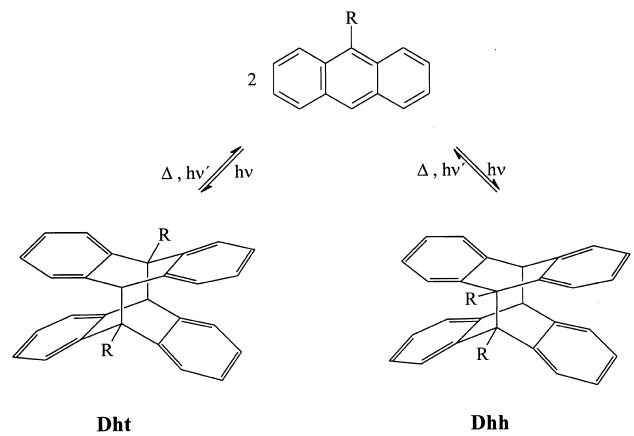
Photodimerization of *n*-alkyl esters of 9-anthracene carboxylic acid was carried out in micellar and vesicular solutions to investigate the influence of the length of the ester chain (C_4–C_{12}) on the ratio Dht/Dhh of formation of the two isomeric products (head-to-tail and head-to-head dimer). With increasing chain length the relative yield of the head-to-head dimer increases. For 9-hydoxymethylanthracene the temperature dependence of regioselectivity in photodimerization was investigated in diethylether, methanol, methylcyclohexane, acetonitrile, and vesicular solutions as solvents. In organic solvents the ratio Dht/Dhh increases with decreasing temperature. In vesicular solution a minimum of the ratio at around 30 °C was found corresponding to a gel-to-liquid-crystal phase transition of the vesicles, which was independently determined by electron spin resonance spectroscopic spin probe technique. © 1997 Elsevier Science S.A.

Keywords: Regioselectivity; Photodimerization; Micelles; Vesicles; Spin probes

1. Introduction

On irradiation 9-substituted anthracenes are known to form two isomeric dimers, the head-to-tail (Dht) and the head-to-head (Dhh) photodimer [1–11] as illustrated in Scheme 1.

Both photodimers can be split thermally and photochemically into the educts, in which the Dhh is the thermodynamically labile product and Dht is stable at room temperature [2,3,10]. It has been shown that regioselectivity in a variety of photodimerizations depends on solvent and temperature [1–3,5,6,8–16]. For 9-hydroxymethylanthracene (HM) in micellar solution it was found that Dhh becomes the major product, a fact which was ascribed to preorientation of the polar HM molecule in the micelles such that the anthracene moiety is directed towards the micelle core and the polar hydroxymethyl group towards the micelle water interface [2,6,9,10]. Since opposite regioselectivity was found in a non-polar reference substance, 9-methylanthracene [3], the conception of preoriented anthracene monomers appeared sound. However, since for 9-methylanthracene there is selectivity in homogeneous solvents, too, and since this selectivity turned out to depend on temperature (distinctly for each solvent), another strong influence on regioselectivity becomes obvious [1], which was ascribed to an equilibration of excimer precursors of Dht and Dhh. These findings made the interpretation of the HM results in micellar solution somewhat equivocal, since the temperature might influence the regioselectivity of HM, too.



Scheme 1. Regioselective photodimerization of 9-substituted anthracenes.

This prompted us to study the temperature dependence of the photodimerization of HM in several homogeneous solvents on the one hand, and in microheterogeneous environments of surfactant vesicles on the other. In these higher selectivity was expected because of the increased rigidity of vesicles as compared with micelles. In addition the dimerization behaviour of some 9-anthracene carboxylic acid esters

* Corresponding author: Tel.: +49 351 463 3633; fax: +49 351 463 3391.

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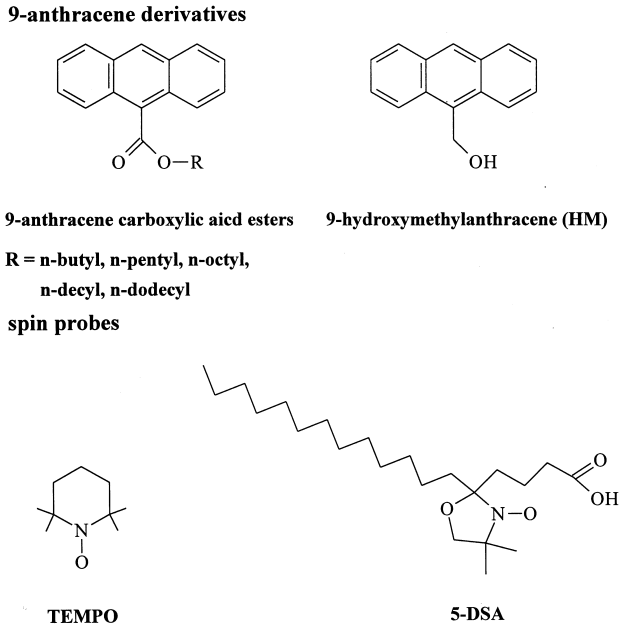

Fig. 1. Structural formulas of anthracene derivatives studied and spin probes used.

with different hydrophobic alkyl chains (see Fig. 1) in micellar and vesicular environment was studied in order to investigate the influence of the length of the chain on the Dht/Dhh ratio. During the investigations electron spin resonance (ESR) spin probe measurements became desirable to understand microenvironmental changes in vesicular solutions.

2. Experimental details

2.1. Substances

Cetyltrimethylammonium bromide, CTAB, (Janssen Chimica, 99+%) was recrystallized from acetone–methanol in a volume ratio of 9:1. 9-Hydroxymethylanthracene, HM, (Lancaster, 99+%) and dioctadecyldimethylammonium bromide, DODAB, (Kodak, p.a.) were used without further purification. The organic solvents, methylcyclohexane, methanol, acetonitrile (all Sigma-Aldrich) and diethylether (Fluka), were used in UV spectroscopic grade. Aqueous solutions were prepared using doubly distilled water.

The esters of 9-anthracene carboxylic acid used in this investigation were prepared as described by Salt and Scott [17]. The esterifications were carried out using the alcohols 1-butanol, 1-pentanol, 1-octanol, 1-decanol and 1-dodecanol (VEB Laborchemie Apolda, distilled before use). After several recrystallization steps the products were identified by ^{1}H NMR and IR spectroscopy.

For ESR spectroscopic measurements the spin probes 2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO, (Lancaster) and 5-(4,4-dimethyloxazoline-3-oxyl)-stearic acid, 5-DSA, (Aldrich) were used without further purification.

2.2. Measurements

Absorption measurements were performed on a homemade UV spectrometer using a PCCD-detector from Alton Instruments Inc. (Lamda Series LS-2000) which is calibrated for wavelengths from 225 to 843 nm. Irradiations were carried out in a thermostatted solidex apparatus using an AMKO 100 W high-pressure mercury lamp (model A1020 with power source LPS 210). 50 ml samples were irradiated through the liquid–air interface. Additionally the samples were stirred during the irradiation. Before irradiation the samples were deoxygenated by bubbling nitrogen for at least 5 min in order to avoid the formation of endoperoxides. Irradiation times were chosen to be 5–10 min to produce dimer yields of about 15%. A filter to cut-off wavelengths below 270 nm was used to excite only the anthracene monomers but not the dimers formed.

To determine the Dht/Dhh ratio three absorption measurements have to be taken. One before and one immediately after irradiation and a third one after keeping the irradiated samples for at least 12 h at 50 °C to ensure complete thermal back reaction of the thermodynamically labile Dhh isomer [3]. From these three spectra the absorption values at the maximum around 370 nm were taken to calculate the Dht/Dhh ratio according to Eq. (1):

$$\frac{\text{Dht}}{\text{Dhh}} = \frac{A_0 - A_R}{A_R - A} \quad (1)$$

where, A_0 is the absorption before irradiation, A the absorption after irradiation and A_R the absorption after thermal back reaction.

The quantum yields for HM in the organic solvents used were determined spectrophotochemically using published values [2] as references.

The ESR spectroscopic measurements were carried out on a Varian ESR spectrometer, model V4500-10A. The microwave frequency was chosen to be 9.81 GHz and the magnetic induction was varied between 3200 and 3400 G. For TEMPO measurements the modulation was set to 100 kHz and the signal gain to 500. For the measurements with 5-DSA the modulation was set to 1000 kHz and the signal gain to 1000. The spectra were recorded with a sweep time between 5 and 15 min for a whole magnetic field sweep.

3. Results

3.1. 9-Anthracene carboxylic acid esters in DODAB vesicles and CTAB micelles

In order to investigate the influence of the length of a hydrophobic chain in 9-position of anthracene, esters of 9-anthracene carboxylic acid and several 1-alcohols have been prepared. The series of esters has been irradiated in vesicular and micellar environment, respectively. Both measurement

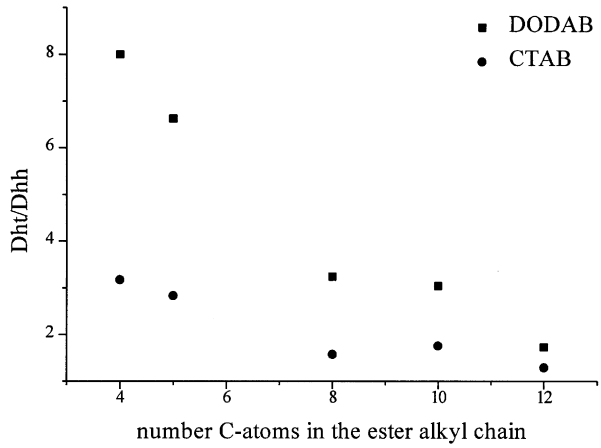

Fig. 2. Dht/Dhh ratio of 9-anthracene carboxylic acid esters as function of the number of carbon atoms in the ester alkyl chain.

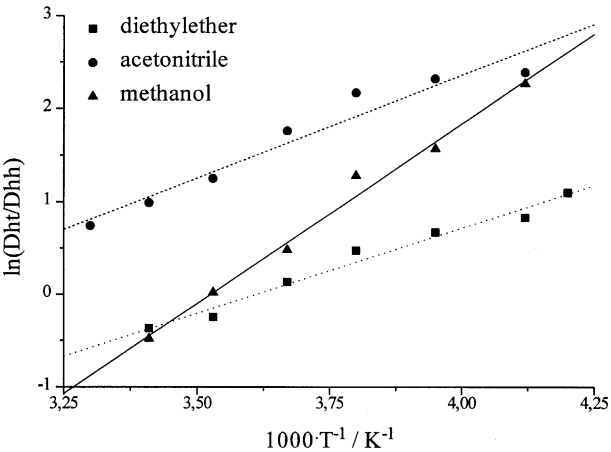

Fig. 3. Dht/Dhh ratio of HM in organic solutions as a function of temperature.

series, in DODAB and CTAB, are combined in Fig. 2. In vesicular as well as in micellar media the amount of head-to-head dimers among the products clearly increased with increasing length of the ester alkyl chain. Even with a dodecyl chain the ratio of head-to-tail over head-to-head dimer is almost 2. So the regioselectivity found with 9-hydroxymethyl-anthracene in microheterogeneous media, where Dhh becomes the major product, could not be reached. Attempts to investigate 9-anthracene carboxylic acid esters with alkyl chains exceeding 12 C atoms failed because the compounds were not sufficiently soluble in the DODAB vesicles nor in the CTAB micelles.

3.2. 9-Hydroxymethylanthracene in homogeneous, organic solution

In Fig. 3 results of irradiations of HM in diethylether, acetonitrile and methanol are shown in the form of plots ln(Dht/Dhh) versus reciprocal temperature (cf. discussion section). A linear dependence is found except for methylcyclohexane. Here the plot exhibits linearity only for the range above 10 °C, while for lower temperatures there is an unexpected high

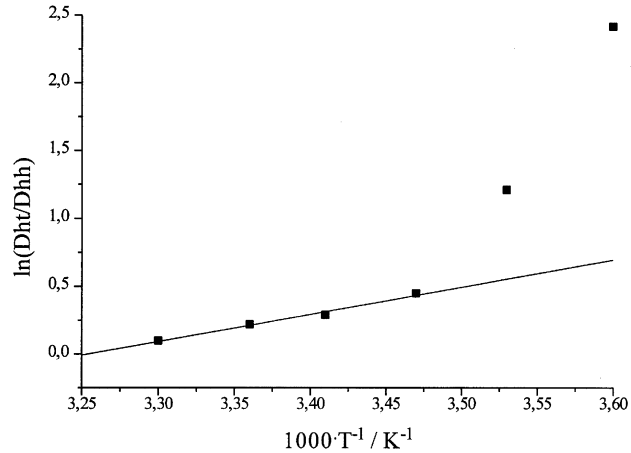

Fig. 4. Dht/Dhh ratio of HM in methylcyclohexane as a function of temperature.

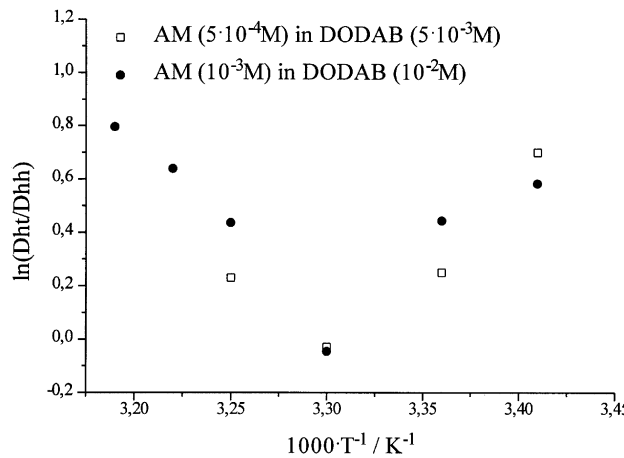

Fig. 5. Dht/Dhh ratio of HM in DODAB vesicles as a function of temperature.

increase in Dht yield with decreasing temperature, as shown in Fig. 4.

3.3. 9-Hydroxymethylanthracene in DODAB vesicles

In the microheterogeneous media of aqueous DODAB solutions, which form vesicles on ultrasonic treatment, the temperature dependence of the Dht/Dhh ratio shows a quite different behaviour. The plots of ln(Dht/Dhh) versus reciprocal temperature clearly exhibit a minimum at around 30 °C with a linear dependence below and above this minimum (Fig. 5).

The temperature at which this minimum occurs approximately corresponds to a phase transition temperature of the DODAB vesicles measured by fluorescence and NMR spectroscopic studies [18–22]. At this temperature, which was determined by Sarpal and Durocher to be 36 °C for DODAB [18], the vesicles undergo a ''gel-to-liquid-crystalline'' phase transition, where the structure of the vesicle bilayer is somewhat softened, resulting in a greater mobility of the surfactant alkyl chains. The gel-to-liquid-crystalline phase

transition is also known for other vesicle forming surfactants [23–28] and was shown to influence reaction rates [29].

3.4. Spin probe measurements in solutions of DODAB vesicles

Since ESR spectroscopic probes should be sensitive to the transition, we were lead to perform spin probe studies in order to prove that the origin of the minimum in the Dht/Dhh ratio of HM in DODAB vesicles at 30 °C is in correspondence to the gel-to-liquid-crystalline phase transition of the vesicles. As described in the literature (e.g. [30] and references cited therein) spin probes can be used to determine microenvironmental changes in surfactant solutions, especially local fluidities. A measure for the mobility of the spin probe is the so called correlation time τ_R which depends on temperature and the viscosity of the immediate environment. The correlation time can be determined using Eqs. (2) and (3) [31]

$$\tau_R = -1.22\times10^{-9}\frac{\mathrm{s}}{\mathrm{G}}b \quad (2)$$

$$\tau_R = 1.19\times10^{-9}\frac{\mathrm{s}}{\mathrm{G}}c \quad (3)$$

where the factors b and c are related to the width and height of the ESR lines

$$b=\frac{1}{2}\Delta B(0)\left(\sqrt{\frac{h_0}{h_{+1}}}-\sqrt{\frac{h_0}{h_{-1}}}\right) \quad (4)$$

$$c=\frac{1}{2}\Delta B(0)\left(\sqrt{\frac{h_0}{h_{+1}}}+\sqrt{\frac{h_0}{h_{-1}}}-2\right) \quad (5)$$

with $\Delta B(0)$ the linewidth of the middle line ($m_I=0$, in Gauss) and h_0, h_{+1}, h_{-1} the signal heights of the lines for $m_I=0, +1, -1$.

This double determination is valid only for correlation times in the range from 5×10^{-11} to 10^{-9} s. Differences in the two determinations result from anisotropy of rotation, molecular arrangement effects or slower rotation ($\tau\geq3\times10^{-9}$ s) of the spin probe. We used the spin probes depicted in Fig. 1.

3.4.1. TEMPO

An ESR spectrum of the spin probe TEMPO in a DODAB solution is shown in Fig. 6 exhibiting a fluid solution spectrum typical for free and isotropic rotation of the spin probe. The evaluation of the spectra recorded at between 20 °C and 40 °C leads to a minimum of the correlation time, which can be determined by linear regression for the parts below and above the minimum as the intersection of the two regression lines. As shown in Fig. 7 this leads to a value of approximately 30 °C for the phase transition temperature of a DODAB solution without a solubilizate added. Fig. 8 exhibits the same temperature dependence of the correlation time for DODAB solution with HM as solubilizate. The intersection

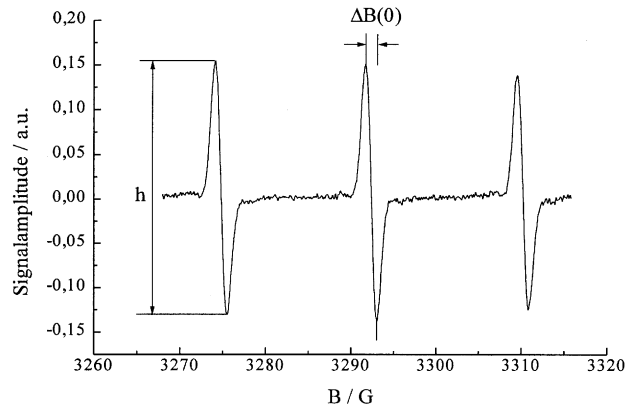

Fig. 6. ESR spectrum of TEMPO in DODAB solution at 26 °C.

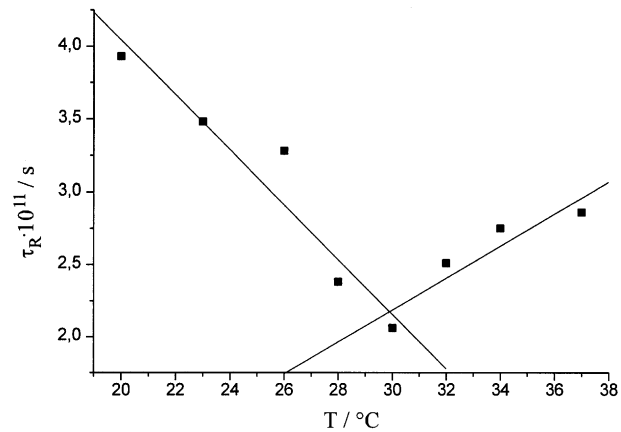

Fig. 7. Correlation times τ_R for TEMPO in DODAB solution.

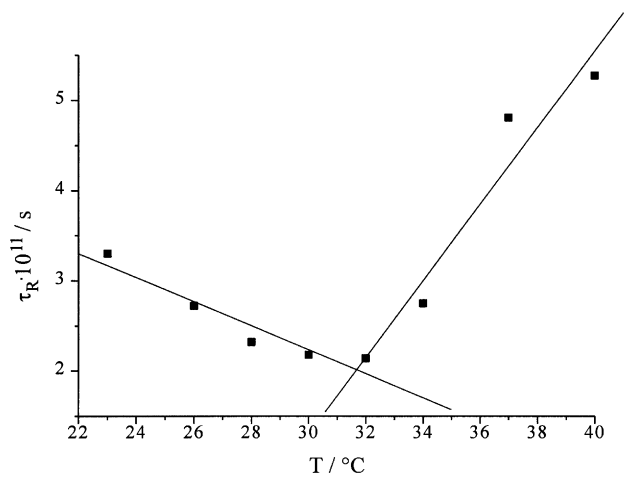

Fig. 8. Correlation times τ_R for TEMPO in DODAB solution containing HM.

of the two regression lines leads to a phase transition temperature for the DODAB vesicles with solubilizate of 32 °C.

3.4.2. 5-DSA

ESR spectra of 5-DSA in DODAB solutions exhibit a different behaviour of this spin probe (see Fig. 9). It can be expected from its structure that 5-DSA is located inside the vesicle, preferably in the outer bilayer volume. The ESR spectra are broadened because of an increased viscosity of

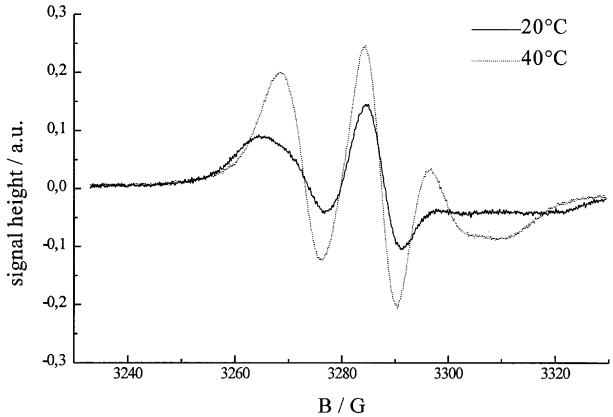

Fig. 9. ESR spectra of 5-DSA in DODAB solution.

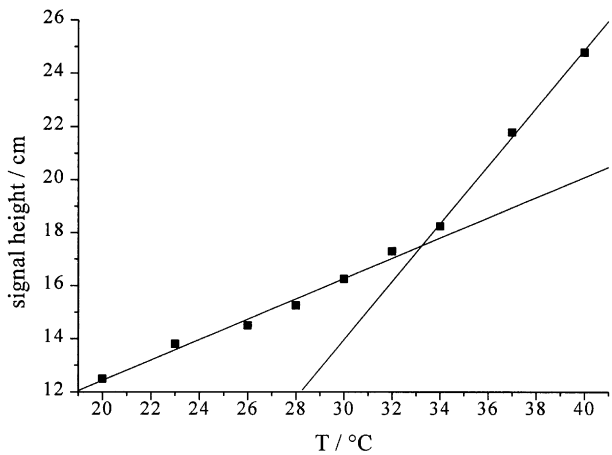

Fig. 10. Signal height of the middle line in the spectra of 5-DSA in DODAB solution.

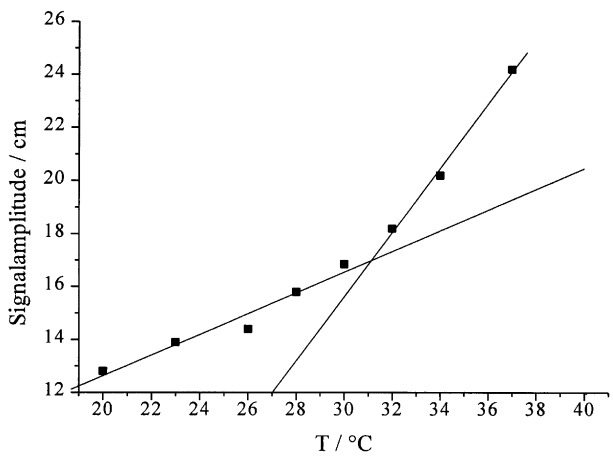

Fig. 11. Signal height of the middle line in the spectra of 5-DSA in DODAB solution containing HM.

the environment of the spin probe and probably because of anisotropic motion. Since the broadening of the spectra prevents an evaluation in the same way as the TEMPO spectra we take the height of the middle line, which increases significantly with increasing viscosity, as an indicative measure for the mobility of spin probe molecules and surfactant alkyl chains inside the micelle. As shown in Fig. 10 the temperature dependence of the line height exhibits two distinct slopes. The phase transition temperature of DODAB vesicles can be determined as the intersection of the two linear regression lines. Thus, Figs. 10 and 11 indicate a phase transition temperature of approximately 33 °C for a pure DODAB vesicle and 31 °C for DODAB vesicles containing HM.

4. Discussion

4.1. 9-Anthracene carboxylic acid esters in DODAB vesicles and CTAB micelles

To understand the influence of the ester alkyl chain on the dimerization behaviour of 9-anthracene carboxylic acid esters it seems to be important to visualize the position of the molecules within the surfactant vesicle membrane. Because of the polarizability of the anthracene moiety and the polarity of the carboxylate group this part of the molecule can be expected localized near the ionic headgroups of the surfactants, whereas the alkyl chain of the ester group is anchored among the surfactant chains in the hydrophobic part of the vesicle and the micelle, respectively. This orientation of the molecules becomes more strict with increasing chain length of the ester alkyl groups and leads to a preorientation of the reactants for photodimerization within the surfactant membrane. Because of this preorientation the plains of the anthracene moieties tend to be perpendicular to the vesicle surface (Scheme 3(a)). Consequently the photodimerization of two neighboured anthracene molecules should favour the formation of Dhh. At shorter alkyl chains (butyl-, pentyl-) a higher selectivity for Dht is found. This may have three reasons, (i) the above mentioned preorientation with anthracene moieties perpendicular to the surface (Scheme 3(a)) might vanish for short chain esters; (ii) the preorientation with the anthracene moieties parallel to (or flat on) the surface (Scheme 3(b)) becomes more favourable for short chain esters; (iii) the molecules are not restricted in their ability of rotation in the excimer state as proposed for 9-methyl-anthracene [1], cf. Scheme 2.

With increasing alkyl chain length the orientation of the 9-anthracene carboxylic acid ester chains parallel to the surfactant alkyl chains becomes more and more rigid leading to an increasing influence of perpendicular preorientation of reac-

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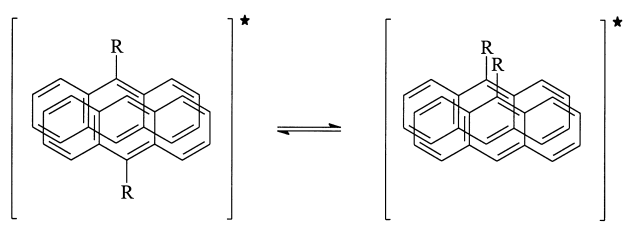
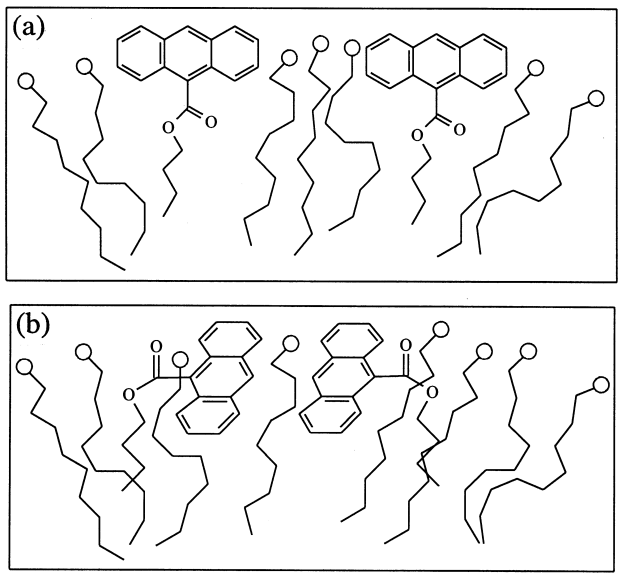


Scheme 2. Excimer precursors in the 9-anthracene photodimerization.



Scheme 3. Illustration of the orientation of 9-anthracene carboxylic acid esters in DODAB vesicles. (a) Anthracene moieties perpendicular to the surface of the vesicle; (b) Anthracene moieties parallel to (or flat on) the surface of the vesicle.

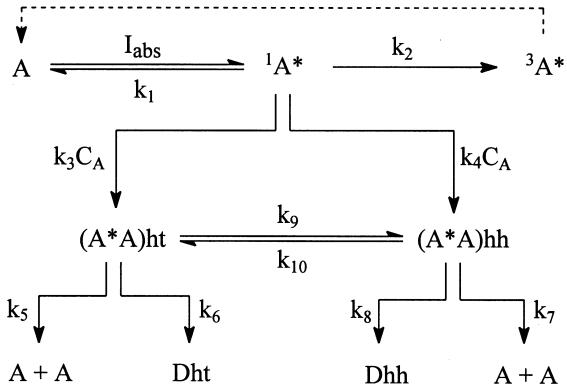
tants in the membrane, which results in a higher yield of Dhh for C_8 and longer ester alkyl chain lengths. But as Dht still is the major product even at C_{12}, there has to be a reason for preferring the Dht as product of photodimerization in common. This reason may be found in the specific orientation of the anthracene carboxylate group in the vesicular/micellar surrounding as illustrated in Scheme 3.

If the carboxylate group is localized between the cationic head groups, the anthracene moieties can assume positions where they lie approximately flat on the surface of the vesicle or micelle or where they are located perpendicular to the surface, as shown in Scheme 3. The parallel position would lead to a head-to-tail photodimerization of two neighbouring monomers, whereas the perpendicular position leads to a head-to-head photodimerization. The results of irradiation of the 9-anthracene carboxylic acid esters support the thesis that the parallel position is occupied by the esters predominantly, but with increasing chain length the perpendicular position becomes more and more important.

As the relative Dhh yields in CTAB solution, compared with DODAB solutions, are generally higher for all alkyl chain lengths, the parallel orientation seems to be unfavourable for the esters in CTAB micelles and the perpendicular orientation is preferred leading to lower Dht yields for 9-anthracene carboxylic acid esters in CTAB micelles compared with DODAB vesicles.

4.2. 9-Hydroxymethylanthracene in homogeneous, organic solution

As described previously the photodimerization of 9-methylanthracene shows a strong temperature dependence in the regioselectivity of the dimer formation [1]. In the reaction



Scheme 4. Reaction pathway of 9-methylanthracene photodimerization.

pathway of the photodimerization of 9-methylanthracene a fast equilibration of the two excimer precursors of the dimers (head-to-tail, **(A∗A)ht**, or head-to-head, **(A∗A)hh**) was established resulting in reaction Scheme 4.

Assuming quasistationarity and $k_3 = k_4$, $k_9 \gg k_5 + k_6$ and $k_{10} \gg k_7 + k_8$ the following expression for the temperature dependence of the quantum yields of head-to-tail (ϕDht) and head-to-head dimer (ϕDhh) formation was derived from Scheme 4 [1]:

$$\ln\left(\frac{\phi\mathrm{Dht}}{\phi\mathrm{Dhh}}\right) = \ln\left(\frac{k_6^0}{k_8^0}\right) - \frac{E_6 - E_8}{RT} + \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (6)$$

where E_i is the activation energy for reaction step i, k_i^0 the frequency factor and ΔS° and ΔH° are the standard entropy and standard enthalpy of formation of the head-to-tail excimer. From Eq. (6) it follows that plots of $\ln(\phi\mathrm{Dht}/\phi\mathrm{Dhh})$, and $\ln(\mathrm{Dht}/\mathrm{Dhh})$, respectively, versus reciprocal temperature should give straight lines [1]. The existence of this excimer equilibrium is supported mainly by two facts: (i) the observed small solvent effects on the dimerization quantum yields (ϕ_D) and (ii) formation of Dhh on irradiation of pure Dht of 9-methylanthracene under conditions where photodimerization of reirradiated anthracene monomers is impossible. While (ii) gives direct evidence for the involvement of an excimer equilibrium, the small changes in ϕ_D (i.e. changes within what can be expected from viscosity variations in the solvents) are a necessary requirement for the validity of Eq. (6).

Fig. 12 shows the temperature dependence of the dimerization quantum yields for HM in the solvents used. As can be seen the requirement of almost agreeing ϕ_D in all solvents is not fulfilled, so that Eq. (6) is not applicable for the evaluation of the photodimerization data of HM. But, as shown in Fig. 3, the linear dependence of $\ln(\mathrm{Dht}/\mathrm{Dhh})$ on the reciprocal temperature appears obvious. Scheme 4 should be the same for 9-methylanthracene and for HM, but for HM because of the polar substituent with the oxygen lone pairs a slower equilibration (k_9, k_{10}) is likely. The quantum yields for Dht and Dhh are given by

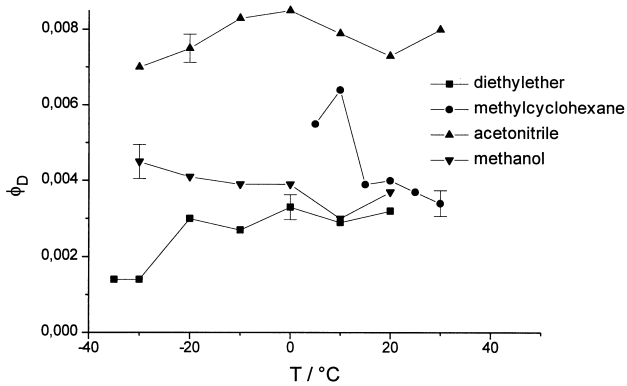


Fig. 12. Temperature dependence of dimerization quantum yields of HM at $C_{HM} = 5 \times 10^{-3}$ mol l^{-1}.

$$\phi\mathrm{Dht} = \left(\frac{k_6}{k_5 + k_6 + k_9}\right)\phi(\mathrm{A^*A})\,\mathrm{ht} \quad (7)$$

$$\phi\mathrm{Dhh} = \left(\frac{k_8}{k_7 + k_8 + k_{10}}\right)\phi(\mathrm{A^*A})\,\mathrm{hh} \quad (8)$$

As the excimer equilibration is assumed to be slow and dimerization quantum yields are low (Fig. 12), the sum of all non reacting deactivations of the excimer, which are comprised in k_5 and k_7, should be fast compared with the dimerization process, which leads to

$$k_5 \gg k_6 + k_9 \text{ and } k_7 \gg k_8 + k_{10} \quad (9a,b)$$

Therefore the ratio of the two dimer quantum yields can be assumed as

$$\frac{\phi\mathrm{Dht}}{\phi\mathrm{Dhh}} \approx \frac{k_6}{k_8}\frac{k_7}{k_5}\frac{k_3}{k_4} \quad (10)$$

Plots of $\ln(\phi\mathrm{Dht}/\phi\mathrm{Dhh})$ versus reciprocal temperature should result in straight lines according to

$$\ln\left(\frac{\phi\mathrm{Dht}}{\phi\mathrm{Dhh}}\right) = \ln\left(\frac{k_6^0 k_7^0 k_3^0}{k_8^0 k_5^0 k_4^0}\right) + \frac{E_8 - E_6 + E_7 - E_5 + E_3 - E_4}{RT} \quad (11)$$

As all plots in Fig. 3 have a positive slope the sum of $E_8 + E_7 + E_3$ has to be larger than that of $E_6 + E_5 + E_4$. This is reasonable since both k_7 and k_3 enlarge the relative yield of Dht under the assumed conditions. With lowering the temperature the reaction steps 3 and 7 seem to overtake step 8 so that the formation of Dhh is suppressed.

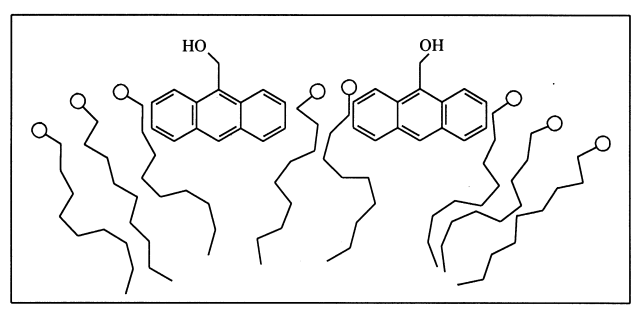
An exact comparison of Figs. 3 and 4 exhibits the smaller temperature range measured for methylcyclohexane. This is because below 5 °C the solubility of HM is too low to perform photodimerizations. Therefore it could be possible that already at below 15 °C HM starts the formation of clusters in methylcyclohexane leading to a sort of ''solid state photodimerization'', which may be an explanation for the strong increase of Dht formation. This assumption is supported by previous results [2] that HM forms hydrogen-bridge-bonded ground state aggregates in apolar solvents leading to aggregates where Dht formation is more likely than Dhh formation as indicated by molecular models. At lower temperature these ground state dimers possibly form clusters with a higher number of aggregated molecules. These clusters would explain the increased dimerization quantum yield below 15 °C (see Fig. 12) in methylcyclohexane because of a greater probability of excimer formation during the lifetime of an excited anthracene monomer. If this is assumed, a linear temperature dependence in methylcyclohexane cannot be expected at 5 and 10 °C (Fig. 4).

Inspection of Fig. 3 shows that the Dht/Dhh ratio is distinct for each solvent at a given temperature. As the plots intersect the sequence of increasing ratios in various solvents may change with temperature. Therefore, no obvious dependence of the Dht/Dhh ratio on solvent parameters like polarity, viscosity or availability of protons is recognisable.

4.3. 9-Hydroxymethylanthracene in DODAB vesicles

In contrast to the acid esters the HM molecule has no alkyl chain which is incorporated in the vesicle interior. However, HM should also occupy a site in the vesicle bilayer which allows a preorientation for Dhh formation: though because of its polarizability the anthracene moiety is located near by the surfactant head groups it can be expected to insert in the bilayer whereas the hydroxy group is polar enough to be located in the electrical double layer of vesicles (see Scheme 5).

As the Dht/Dhh ratios for HM are much lower than for all of the acid esters so that Dhh becomes the major product, the preorientation of HM molecules in the head group region of the vesicle bilayer seems to be more uniform than that of acid esters. This preorientation is lost more and more above the vesicle phase transition temperature due to greater mobility. Thereby Dht formation is favoured as in homogeneous solvents. In addition the improved fluidity of the bilayer enables anthracenes originally located at the inner and outer surface of the bilayer, respectively, to ''find'' each other during the lifetime of an excited molecule leading to preferred Dht formation. An explanation of the decrease in Dhh yield below the phase transition temperature must be less straight forward. Because of the rigidity of the surfactant alkyl chains in the gel state the anthracene molecules may be pushed out of the bilayer to the more fluid head group region, whereby the preorientation diminishes.



Scheme 5. Illustration of the orientation of HM in DODAB vesicles.

4.4. Spin probe measurements in solutions of DODAB vesicles

The two different spin probe measurements lead to apparently different effects of HM solubilization (increase and decrease of the phase transition temperature). The spin probes, however, differ in the exact location of the probing NO group in the vesicle solution. Owing to its molecular structure, the NO group of 5-DSA is located inside the vesicle and is therefore detecting changes in the bilayer structure right where they occur. But the spin probe molecules distort the surfactant alkyl chain order and are only able to measure changes at the locus of this distortion. Moreover, an exact evaluation of the 5-DSA data would require complicated simulations of ESR spectra. Since we observe only one triplet ESR signal TEMPO is located in the electrical double layer of the vesicle (in contrast to the expectation of a distribution of TEMPO between the vesicle and the water phase as described by Marsh [31]). The position of the spin probe molecules, however, is close enough to the alkyl chains to detect changes in the bilayer structure without distorting the surfactant molecules. Therefore, the TEMPO data appear more reliable. The solubilization of HM, thus, seems to have a slight increasing influence on the phase transition temperature, which agrees well with the minimum of the Dht/Dhh ratio in Fig. 4.

5. Conclusion

It has been shown that in 9-anthracene carboxylic esters longer ester chains (C_4–C_{12}) have the expected influence on the photodimerization regioselectivity, i.e. the relative amount of Dhh formation is increased. Generally the preorientation of reactants in microheterogeneous solutions has an important influence on the regioselectivity, which in HM depends on the order of the vesicle phase. Preorientation is, however, not the only influencing factor on the photodimerization of 9-substituted anthracenes in micellar and vesicular solution. Mainly temperature effects—also affecting Dht/Dhh ratios in homogeneous solutions—have to be considered, which can be rationalised by a rather complicated kinetic reaction scheme.

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