

PHOTOCHEMICALLY INDUCED VISCOSITY CHANGES IN MICELLAR CETYLTRIMETHYLAMMONIUM BROMIDE SOLUTIONS CONTAINING 4-HYDROXYSTILBENE

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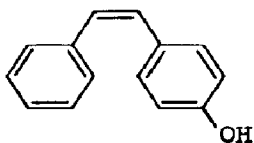
Summary

The dynamic viscosities of solutions containing 0.25 M cetyltrimethylammonium bromide and various concentrations of 4-hydroxystilbene or azobenzene were measured. The viscosity increased with solubilizate concentration. This effect was more pronounced in *cis*-4-hydroxystilbene than in the *trans* compound. Accordingly, photochemical *cis*-*trans* and *trans*-*cis* isomerizations of 4-hydroxystilbene performed *in situ* can be used to alter the viscosity of the solution. Photoisomerizing azobenzene has no effect on the viscosity in the concentration range investigated (below 10 mM).

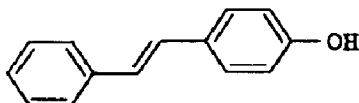
1. Introduction

Recently we have shown that the viscosities of micellar solutions are greatly increased by solubilization of certain aromatic compounds whereas other aromatic compounds do not show this effect [1, 2]. The photochemical transformation of compounds belonging to the former class into substances belonging to the latter (and vice versa) resulted in corresponding changes in the viscosities ("photorheological effect"). Previously, the reversible *cis*-*trans* isomerization of some azobenzenes has been reported to have large effects on the light transmission and the electrical resistance of certain microemulsions and membrane systems [3, 4]. It is believed that these phenomena are due to conformational changes induced by the solubilization of the light-absorbing species present in the molecular organizations existing in the solutions.

In this paper we describe the influence of solubilized 4-hydroxystilbene (HS)



cis-4-Hydroxystilbene (cHS)



trans-4-Hydroxystilbene (tHS)

and its photoisomerization on the viscosities of aqueous micellar solutions of cetyltrimethylammonium bromide (CTAB). For comparison, further experiments were carried out using azobenzene as a solubilizate. The photochemistry of stilbenes has already been investigated thoroughly: in dilute solutions the dominant photoreactions are *trans*-*cis* and *cis*-*trans* isomerizations [5]. Upon prolonged irradiation, mixtures of *cis*- and *trans*-stilbene are obtained containing photostationary concentrations of the isomers according to

$$\frac{c_c}{c_t} = \frac{\epsilon_t(\lambda)\Phi_{tc}}{\epsilon_c(\lambda)\Phi_{ct}}$$

where c_c , c_t denote the concentrations of *cis*- and *trans*-stilbene, ϵ_c , ϵ_t the corresponding absorption coefficients and Φ_{ct} , Φ_{tc} the quantum yields for *cis*-to-*trans* isomerization and *trans*-to-*cis* isomerization respectively. For instance, irradiation with light of wavelength $\lambda = 313$ nm yields a *cis*-rich (up to 90%) mixture while at $\lambda = 254$ nm the photostationary equilibrium contains comparable concentrations of *cis*- and *trans*-stilbene. In competition with isomerization, *cis*-stilbenes form phenanthrenes [6, 7] in the presence of hydrogen acceptors (O_2 , I_2). At high stilbene concentrations photodimerization of *trans*-stilbene leads to isomeric tetraphenylcyclobutanes [8] which are thermally stable at room temperature. The photodimerization can be reverted by irradiation at wavelengths around 250 nm.

2. Experimental details

CTAB (Merck, pro analysi), azobenzene (Fluka, better than 98%) and tHS (Janssen Chimica, better than 98%) were used as supplied.

Micellar solutions containing solubilizates were prepared as described previously [9].

Irradiations at $\lambda = 313$ nm and at $\lambda = 254$ nm were performed in cylindrical quartz cuvettes ($\phi = 1.5$ cm; $d = 2$ cm) using a high pressure mercury lamp and interference filters. During the irradiations (3 - 5 h) the solutions were stirred and kept under an argon atmosphere.

A *cis*-rich mixture of cHS and tHS was prepared by irradiation with Pyrex-filtered light of 500 ml of a solution of tHS in methanol (0.05 M) for 7 h at 20 °C in a falling film apparatus using a 125 W high pressure mercury lamp. The solvent was evaporated and the residue analysed by proton nuclear magnetic resonance (1H NMR) spectroscopy using a Bruker WP 80 spectrometer. Assignments of 1H NMR absorptions were made according to ref. 10. The mixture contained cHS and tHS in a ratio of about 7:3 and less than 1% phenanthrene. In an analogous irradiation of 0.01 M tHS in 0.25 M aqueous CTAB for 5 h, a higher *cis*-to-*trans* ratio (about 9:1) was obtained. That there were no traces of tetraphenylcyclobutanes was indicated by the absence of 1H NMR signals around 4.4 ppm [11]. For quantitative analyses 1H NMR spectroscopy was used because UV-visible absorption data of HS

in the solvents employed are not reported in the literature. Only extinction coefficients in ethanol are given in ref. 12.

Absorption spectra were recorded using a Beckman Acta M VII spectrometer and were used for obtaining qualitative information.

Dynamic viscosities were measured at 25 ± 0.2 °C using Ostwald viscometers. No measurable deviation from Newtonian flow behaviour was observed.

3. Results

Despite numerous investigations on stilbenes very few papers deal with the photochemistry of HS (see for instance ref. 12). Therefore the photochemistry of HS was briefly investigated in dilute solutions (about 1.5×10^{-5} M) of tHS in methanol and in aqueous 0.25 M CTAB. tHS was irradiated at a wavelength of 313 nm and the reaction was followed by UV spectroscopy. The absorption spectrum of tHS in methanol showed a minimum at 248 nm, maxima at 226 and 303 nm and a shoulder at 310 nm. It is similar to spectra of other *trans*-stilbene derivatives published in the literature [5, 10, 12]. Upon irradiation the spectrum changed gradually up to a final shape exhibiting maxima at 227 and 291 nm and a minimum at 248 nm as in the analogous absorption spectrum of *cis*-stilbene [5]. The spectra also roughly agree with those reported by Schmid for cHS and tHS in ethanol [12]. Reirradiation of the solution at $\lambda = 254$ nm was followed by a partial reversion of the photoreaction. All spectra passed through an isosbestic point at $\lambda = 267$ nm. These observations are in keeping with the occurrence of *trans*-*cis* and *cis*-*trans* isomerizations as in other stilbene derivatives [5]. The decomposition of HS reported [12] to occur upon polychromatic irradiation in ethanol was not observed under our reaction conditions.

The UV spectrum of tHS in 0.25 M aqueous CTAB (maxima at 227 and 320 nm, shoulder at 310 nm, minimum at 250 nm) differed from that in methanol with respect to the structure of the low energy absorption band. This band in CTAB shifts to longer wavelengths by about 10 nm and the order of position of the maximum and the shoulder changes. Similar phenomena are observed when the spectra of tHS in neutral and alkaline (pH 12) water are compared: at neutral pH the maximum and the shoulder appear at 300 nm and 315 nm respectively, while at pH 12 a shoulder (321 nm) appears at higher energy than the maximum (340 nm). At high pH the spectral changes in water can be attributed to the formation of stilbenolate anions. It follows from the similar shape of the spectrum in CTAB that ion pairs of cetyltrimethylammonium cations and stilbenolate anions are formed when HS is associated with micelles. However, the photochemistry in CTAB is similar to that in methanol: a *cis*-stilbene-like spectrum is obtained when tHS in CTAB is irradiated at $\lambda = 313$ nm (maxima at 227 and 294 nm, minimum at 250 nm). When such a solution was reirradiated at

$\lambda = 254$ nm the photoreaction was partly reversed. The products formed in the preparative irradiations in CTAB and in methanol differed in that a larger cis-to-trans ratio was obtained with CTAB as the solvent. Despite the high local concentrations of HS in CTAB no tetraphenylcyclobutanes (and only trace amounts of phenanthrene) were detected in the reaction mixtures.

The dynamic viscosities of aqueous solutions containing 0.25 M CTAB and between 0.5 and 10 mM tHS were measured. The viscosity increases with the concentration of tHS from 1.79 mPa s (pure 0.25 M CTAB) to 2.57 mPa s at 9.99 mM tHS. A more pronounced increase in viscosity (up to 3.22 mPa s at 10.1 mM HS) was found when analogous experiments were performed using cis-rich HS (about 70% cis), which was prepared from tHS in methanol using Pyrex-filtered radiation. The dependence of the viscosity on the concentration of tHS and of cis-rich HS is displayed by the full and the broken curves in Fig. 1.

The viscosities of the solutions were changed *in situ* by irradiating them in a quartz cuvette at 313 and 254 nm. For instance, the viscosities of solutions containing 4.82 mM and 7.36 mM tHS changed from 2.00 to 2.16 mPa s and from 2.28 to 2.71 mPa s respectively when irradiated at 313 nm until a constant viscosity was attained. The viscosity increase of the irradiated micellar solutions as well as of solutions of the externally prepared cis-rich HS could be reversed to some extent by reirradiation at 254 nm. These irradiations were not carried out to constant viscosity because the intensity of the irradiation source was too low at 254 nm and because the thermal cis-trans isomerization may interfere at longer irradiation times: a

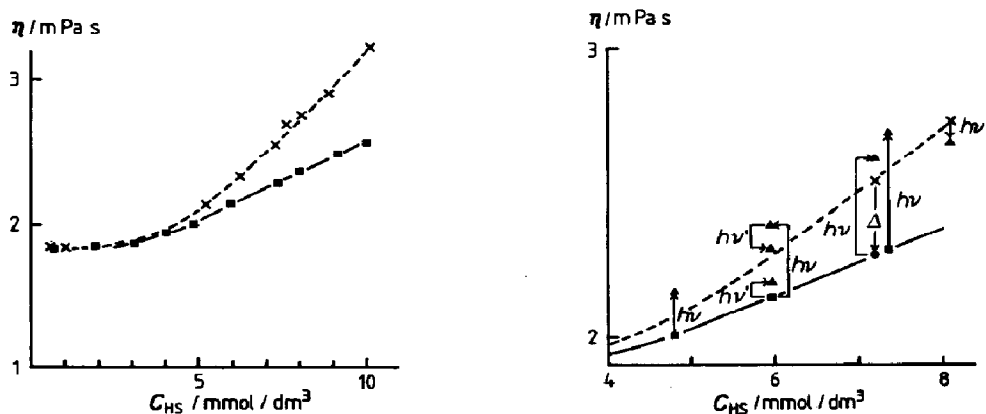


Fig. 1. Dynamic viscosity η at 25 °C of aqueous solutions containing 0.25 M CTAB as a function of the concentration C_{HS} of solubilized HS: \blacksquare , tHS; \times , cis-rich (about 70%) mixture of cHS and tHS.

Fig. 2. Photochemically and thermally induced viscosity changes in aqueous solutions containing 0.25 M CTAB and various concentrations C_{HS} of HS at 25 °C. The solid and the broken lines and the symbols \blacksquare and \times coincide with those of Fig. 1. $h\nu$ and $h\nu'$ refer to irradiations at $\lambda = 313$ nm and at $\lambda = 254$ nm respectively, and Δ refers to storage of the sample at about 25 °C for 1 week. \blacktriangle , \bullet : values reached after irradiation and after thermal reaction respectively.

slow thermal back reaction (previously reported by Schmid [12]) in the solutions of cis-rich HS (not in the solid material) was indicated by the UV spectrum and resulted accordingly in a decrease in viscosity over several days. The thermal back reaction in turn can be reversed by further irradiation at $\lambda = 313$ nm. Figure 2 illustrates the results of some of these photochemical and thermal experiments.

In the presence of azobenzene as a solubilize the viscosity of a 0.25 M aqueous CTAB solution increases at a rate similar to that of HS: solutions containing 2.15, 4.41, 6.95 and 9.03 mM azobenzene had viscosities of 1.91, 2.04, 2.31 and 2.61 mPa s at 25 °C. However, changing from trans-rich to cis-rich azobenzene and vice versa (*i.e.* irradiating at $\lambda = 366$ nm and $\lambda > 420$ nm) had no significant effect on the viscosity.

4. Discussion

Previously [1, 2] the increase in the viscosity of micellar solutions in the presence of aromatic solubilizes has been attributed to the induced formation of larger colloidal particles, *i.e.* rod-like micelles, within a concentration range in which only spherical micelles would be present in the absence of solubilizes. This is the case at 0.25 M CTAB [13]. In the case of solubilized 9-anthracene carboxylic acid it was shown that the acid is highly dissociated in CTAB solutions [14] so that the anions can replace the bromide counter-ions of the micelles. It is well known that large and strongly binding counter-ions induce rod formation [15] and the presence of anisometric particles in dilute CTAB solutions containing 9-anthracene carboxylic acid has been proved by means of low angle light-scattering experiments [16]. Similarly, stilbenolate anions may replace some of the bromide counter-ions thereby inducing the growth of micelles since at least the partial formation of ion pairs is indicated by the UV spectra of HS in aqueous CTAB. In this respect cHS seems to be more efficient than the trans isomer as the viscosity rises upon changing the solubilize from tHS to cHS either photochemically *in situ* or by solubilizing tHS and cis-rich HS separately. The higher efficiency of the cis isomer in raising the viscosity seems to be due to stronger binding of its anions to cetyltrimethylammonium cations.

The results also show that the conformational change associated with the isomerization has no considerable effect on the viscosity. This follows from the viscosity data obtained with azobenzene as a solubilize. The rheological effect of solubilized azobenzene turns out to be even slightly larger than that of tHS. However, the viscosities of micellar solutions of *cis*- and *trans*-azobenzene appear to be the same, *i.e.* the photorheological effect that might have been expected on the basis of previous work [3, 4] was not detected.

That the HS viscosities reached upon performing *in situ* irradiation at $\lambda = 313$ nm are higher than those obtained with the externally isomerized

material can be ascribed to the fact that the photostationary cis-to-trans ratio on 313 nm irradiation in CTAB is higher than on irradiation in methanol using polychromatic Pyrex-filtered light (*cf.* Section 2).

The effects of the hydroxystilbenes on the viscosities of CTAB solutions are shown to be much smaller than those of the anthracene derivatives investigated previously [1, 2]. Their photochemical transformations (dimerization and endoperoxide formation) lead to completely inefficient compounds while both HS isomers are rheologically active. The photoisomerization of the hydroxystilbenes is, however, an inherently much simpler process which is more easily reversed. This may in turn be decisive in any application of photochemical flow control.

5. Conclusion

The viscosity of aqueous CTAB solutions containing HS can be increased or decreased *in situ* by photochemical trans-cis and cis-trans isomerization. This photorheological effect deserves some study in view of possible applications based on simple viscosity measurements, such as actinometry and the measurement of the kinetics of micelle formation.

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