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SHORT COMMUNICATION

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Influence of solubilized stilbene derivatives in *trans* and *cis* configuration on the phase equilibrium hexagonal – isotropic in potassium octanoate – water systems: Light-induced isothermal switching of clearing points

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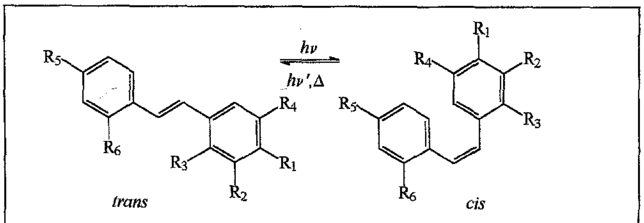
Abstract Clearing temperatures T_{HI}, as observed in phase transitions from the hexgonal lyotropic liquid crystalline phase to the isotropic micellar phase of aqueous potassium octanoate systems were found to be sensitive to the presence of small amounts of certain stilbene derivatives. The influence on T_{HI} is specific for the stilbene derivative and depends on whether the *cis* or *trans* form is present. Since *trans* and *cis* isomers can be interconverted photochemically, phases can be switched *in situ* upon exposure to light. Eight derivatives of stilbene were tested: 4-hydroxystilbene, 4-potassium-stilbenolate, 3- and 4-carboxystilbene, 3- and 4-potassium stilbene carboxylate, 2′,5′-dimethoxy-4-aminostilbene, and 4,4′-diaminostilbene-2,2′-disulfonic acid. Upon solubilizing $\leq 1\%$ w/w of trans stilbenes the clearing points varied between $+15.5$ K to -12 K as compared to pure aqueous potassium octanoate. Photoisomerization to the cis form resulted in increases of T_{HI} by up to 7.5 K.

Key words Lyotropic liquid crystals – phase transitions – photoisomerization – solubilization

Introduction

In various lyotropic liquid crystalline (LLC) surfactant systems photochemically triggered phase transitions were found which were brought about by photoreactions of certain solubilized aromatic compounds as reviewed in [1]. Among the surfactant systems investigated there was aqueous potassium myristate in which a stilbene derivative, 4-hydroxystilbene (**4HS**), induced an increase of the clearing temperature T_{HI} (from the hexagonal to the isotropic phase) when solubilized at $< 1\%$ w/w in its *trans* form. A further increase by several degrees was observed upon transforming *trans* **4HS** to *cis* **4HS** photochemically. Thus a photochemically induced phase transition hexagonal → isotropic was possible when samples were irradiated at temperatures close to the phase equilibrium [2].

In this study we report the influences of solubilizates and their photoisomerization on the phase equilibrium hexagonal – isotropic in potassium octanoate (**KO**), which is the fatty acid salt with the shortest alkyl chain out of the ones forming micellar systems. It was chosen since a previous study [2] had suggested that in systems of smaller micelles greater effects on T_{HI} might be expected due to more intense interfering of solubilizates with the packing of surfactant monomers. Eight stilbene derivatives (capable of photochemical *trans-cis* isomerization, Fig. 1) were selected for the investigation, since the stilbene photoisomerization involves the sort of change in molecular shape which is likely to affect phase equilibria in LLC systems, cf. [2, 3]. Variations of the functional groups attached to the stilbenes will be shown to have an additional specific influence.



4-HS: R_1 = OH, R_2-R_6 = H
4-KS: R_1 = OK, R_2-R_6 = H
4-CS: R_1 = COOH, R_2-R_6 = H
4-KCS: R_1 = COOK, R_2-R_6 = H
3-HS: R_1,R_3-R_6 = H; R_2 = COOH
3-KCS: R_1,R_3-R_6 = H; R_2 = COOK
DMAS: R_1,R_2,R_6 = H; R_3,R_4 = OCH_3; R_5 = NH_2
DASDS: R_1,R_5 = NH_2; R_2,R_4 = H, R_3,R_6 = SO_3H

Fig. 1 Photoisomerization of the stilbene derivatives investigated

Experimental section

Materials

Potassium octanoate (**KO**): 1.5 dm^3 of a 3 molar solution of KOH in ethanol was added to a solution of 500 g (3.47 mol) octanoic acid in 1 dm^3 of absolute ethanol. After refluxing this mixture for 2 h 1 dm^3 of dry acetone was added. Upon cooling to room temperature **KO** precipitated in the form of colorless plates which were recrystallized four times from ethanol/acetone and washed with two times 500 ml of dry acetone. The product was dried *in vacuo* at 100 °C for 5 h. IR spectra revealed the absence of OH groups in the product. Yield: 74%.

4-Hydroxystilbene (**4HS**) was available from a previous investigation [2]. 4-Potassium stilbenolate (**4KS**) was prepared from **4HS** (10 g dissolved in absolute ethanol) by reaction with potassium hydroxide (1 molar in dry ethanol, added dropwise) under boiling condition. Upon cooling to room temperature **4KS** precipitated (6.5 g, 54.5%, of fine white crystals, mp 230 °C, decomp.) and was recrystallized from dry ethanol.

3- and 4-carboxystilbene (**3CS, 4CS**) were left from another previous study [3]. The potassium salts of these acids (**3KCS, 4KCS**) were prepared as follows: to a solution of 5 g (22 mmol) of 3- or 4-carboxy stilbene in 50 ml absolute ethanol at 50 °C 30 ml of a solution of KOH in ethanol was added dropwise. Upon cooling the potassium salts precipitated. They were separated and recrystallized twice from absolute ethanol to yield 4.2 g (16 mmol, 73%) of **4KCS** (mp $>$ 380 °C) and 2.8 g (11 mmol, 50%) of **3KCS** (mp 295–300 °C).

2′,5′-Dimethoxy-4-aminostilbene (**DMAS**) and 4,4′-diaminostilbene-2,2′-disulfonic acid (**DASDS**) were purchased from Janssen Chimica and purified by two recrystallizations from ethanol.

Sample preparation

Triple distilled water and the desired chemicals were weighed in 10 ml glass vials which were sealed, and the mixture was stirred until homogeneity at 60 –70 °C.

Clearing temperature determination

Samples inside a thermostatted cell of 1 mm optical path length (described earlier [2, 3]) were placed between crossed filters for linearly polarized light. Light of a Helium-Neon Laser (not absorbed by stilbenes and surfactants) only passed through filters and samples when an anisotropic (i.e., hexagonal) phase was present which converts lineraly polarized to elliptically polarized light. Starting in the isotropic phase clearing points were determined by lowering the temperature in intervals of 0.1 K until laser light passing the apparatus was detected (visually on a screen or by means of a photodiode).

Irradiations

UV irradiation of samples containing *trans* stilbenes was performed using the apparatus for clearing point determination described above. Appropriately filtered light of a 100 W high pressure mercury lamp was directed on the samples collinearly with the phase detection laser. Wavelengths were selected such that the surfactant was not and the *trans* stilbenes were irradiated in the long wavelength tail of their absorption spectra. This procedure leads to *trans-cis* conversion of between 80 and 95%, cf. [2, 3] (for a review on the photoisomerization of stilbenes see [4]).

Polarizing microscopy

The hexagonal structure of lyotropic liquid crystalline phases were checked by the texture of the samples on a polarizing microscope (Nikon Optiphot 2).

Results

The published ternary phase diagram (**KO**-decanol-water [5]) reveals the formation of a hexagonal phase in the binary system potassium octanoate (**KO**)-water at **KO** concentrations above 43% w/w, i.e., at $\{100\, m(\mathbf{KO})/[m(\mathbf{KO}) + m(\text{water})]\} > 43$ with m denoting masses of ingredients. In this concentration range we determined clearing points T_{HI} marking the equilibrium between the

Table 1 Clearing temperatures T_{HI} of pure aqueous surfactant systems, $T^{\mathrm{s}}_{\mathrm{HI}}$ in the presence of solubilizates in the *trans* form, and T^{*}_{HI} after photochemical conversion of solubilizates to the *cis* form

Solubilizate	KO concentration/ % w/w	Solubilizate concentration/ % w/w	T_{HI}/°C without solubilizate	$T^{\mathrm{s}}_{\mathrm{HI}}$/°C with solubilizate	T^{*}_{HI}/°C with solubilizate irradiated
–	43.25	–	26.0	–	–
–	43.50	–	37.0	–	–
–	43.75	–	47.5	–	–
–	44.00	–	57.0	–	–
–	44.25	–	67.0	–	–
4HS	43.50	1.0	37.0	38.5	46.0
4KS	43.50	1.0	37.0	43.5	48.5
4CS	43.50	1.0	37.0	35.0	42.0
4KCS	43.50	1.0	37.0	52.0	57.0
3CS	43.50	1.0	37.0	52.5	52.7
3KCS	43.50	1.0	37.0	54.0	54.0
DMAS	44.00	1.0	57.0	66.0	69.0
DASDS	44.00	0.5	57.0	45.0	48.0

isotropic solution and the upper border of the two-phase region (isotropic/hexagonal liquid crystals). Since the binary phase diagram is not published, the width of this two-phase region is not known, and our apparatus cannot distinguish anisotropic one and two-phase regions. Generally these regions are quite wide in aqueous potassium soaps [6]. Values for T_{HI} are listed in Table 1. The phase equilibrium temperature between the isotropic solution and the hexagonal phase rises very steeply with increasing **KO** concentration. Therefore measured T_{HI} values are very sensitive to errors in the sample composition, so that the values are reproducible within ± 0.5 K only. The addition of solubilizates did not change the structure of the lyotropic liquid crystalline phase as revealed by the textures obtained from a polarizing microscope which are in keeping with a hexagonal phase structure [7].

Results of clearing point determinations in the presence of solubilizates are comprised in Table 1. In the table concentrations of solubilizates are given in % w/w, i.e., 100 m(solubilizate)/[m(solubilizate) + m(**KO**) + m(water)]. Inspection of the table reveals that the solubilization of *trans* stilbenes influences the stability of the liquid crystalline hexagonal phase, i.e., **4CS** and **DASDS** lower the clearing point while the other solubilizates increase it. The most pronounced influence is exhibited by **DASDS** which at 1% w/w completely suppresses the formation of the hexagonal phase in 44% **KO**. The potassium salts always induce a higher transition temperature as compared to the corresponding phenol or acids. Irradiation, i.e., conversion of *trans* isomers to *cis* isomers, leads to an increase of T_{HI} by 3 to 7 K, except for **3CS** and **3KCS**.

Whenever irradiation increases T_{HI} an isothermal switch from the isotropic to the hexagonal phase upon irradiation is possible. For these experiments samples were thermostatted at a temperature between $T^{\mathrm{s}}_{\mathrm{HI}}$ in the presence of the non irradiated solubilizate and T^{*}_{HI} of the irradiated system, i.e., in the isotropic phase near the transition temperature. After a few minutes of irradiation of such thermostatted samples the anisotropic phase was detected. Switching times depended on the difference between the irradiation temperature and $T^{\mathrm{s}}_{\mathrm{HI}}$, and on the intensity of the irradiation light.

Upon storing irradiated systems at the irradiation temperature for a couple of days (depending on irradiation time and stilbene derivative) the isotropic phase reappeared due to thermal re-isomerization from the *cis* form to the *trans* form. The re-isomerization time can be reduced to a few hours by heating the samples to 65 °C. In this way switching of phases was cycled several times without changes of $T^{\mathrm{s}}_{\mathrm{HI}}$ and T^{*}_{HI}.

Discussion

In **4KS**, **3KCS**, and **4KCS** the stabilization of the hexagonal phase upon solubilization is drastically more pronounced as compared to the corresponding acidic solubilizates. This may be ascribed to the increase of electrolyte present in the systems when the potassium salts dissociate to a significantly higher degree as compared to the acidic and phenolic analogues.

The fact that $T^{\mathrm{s}}_{\mathrm{HI}}$ and T^{*}_{HI} are not changed upon repeated photoisomerization indicates that *trans-cis* isomerization of the stilbenes is the dominating process occurring. Possible side-reactions, i.e. photodimerization [8] and photocyclization [9], obviously are less important as compared to photoisomerizations of **3CS** and **4CS** in cationic cetyltrimethylammonium bromide systems [3].

Generally, the efficiency of bimolecular photodimerizations is increased in micellar systems [1] since due to solubilization in micelles the concentration of reactants is enhanced locally. In the anionic surfactant systems investigated here high pH values dominate, so that the acidic solubilizates may be present in their dissociated ionic form disfavoring dimerization due to electrostatic repulsion. The potassium salts of the solubilizates – not investigated previously – can also be expected to dissociate upon solubilization. For practical purposes, however, the number of possible switches must be determined, since irreversible side-reactions – even at low quantum yields – will consume the photoreactive material upon repetition of reaction cycles, cf. [3].

The difference of 7.5 K between T^{*}_{HI} and $T^{\mathrm{s}}_{\mathrm{HI}}$ observed here for **4HS** in potassium octanoate **KO** is ca. two times the difference obtained in analogous potassium myristate systems while in potassium oleate there is no change of T_{HI} upon photochemical conversion of *trans* to *cis* **4HS** [2]. The diameter of micellar aggregates increases with the surfactant alkyl chain length. This influences the extent of interactions that conformational changes of solubilizates can have with the packing of the surfactant monomers in the aggregates. These interactions should increase with the size ratio of solubilizate and surfactant as corroborated by the results.

The general observation [1, 2, 3, 10–12] that oblong solubilizate molecules (such as *trans* stilbenes) induce lower transition temperatures than more spheric ones (e.g. *cis* stilbenes), i.e., that the latter ones stabilize the anisotropic phase, is resembled by the systems investigated here with the exception of **3CS** and **3KCS** in which photoisomerization does not lead to significant effects on T_{HI}. We may discuss that **3CS** and **3KCS** deviate from an oblong shape already in the *trans* form when compared to **4CS** and **4KCS**. This should, however, also hold for **DASDS**. Moreover, in aqueous cationic cetyltrimethylammonium bromide the photochemical *trans* – *cis* isomerization of **3CS** was more efficient in increasing transition temperatures as compared to **4CS** [3]. Obviously the shape of the solubilizate is only one out of a variety of factors affecting phase equilibria in lyotropic liquid crystalline surfactant systems.

DASDS in both *trans* and *cis* form decreases drastically the phase transition temperature, i.e., the LLC phase is destabilized. The formation and destruction of the hexagonal LLC phase can be initiated by two processes [13]: i) elongation/shortening of rod-like micellar aggregates and ii) increase/decrease of the rod flexibility. Here, **DASDS** may increase the flexibility of octanoate rods since it exists in its dianionic form in the alkaline systems. When and where incorporated in anionic micelles these dianions can displace surfactant head groups, thereby increasing inter-head-group distances locally and inducing a bending of the aggregate. Solubilization of **DASDS** in the bulk aqueous phase is less likely since in that case it would act as added electrolyte which generally stabilizes anisotropic phases.

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References

1. Wolff T, Klaussner B (1995) Adv Colloid Interface Sci 59:31
2. Klaussner B, Nees D, Schmidt F, Wolff T (1994) J Colloid Interface Sci 162:481
3. Wolff T, Seim D, Klaussner B (1991) Liq Cryst 9:839
4. Waldeck DH (1991) Chem Rev 91:415
5. Ekwall P, Mandell L, Fontell K (1969) J Colloid Interface Sci 31:508
6. McBain JW, Sierichs W (1948) J Am Oil Chem Soc 25:221
7. Roosevear FB (1954) J Am Oil Chem Soc 31:628
8. Lewis FD (1986) Adv Photochem 13:165
9. Bromberg A, Muszkat KA, Fischer E (1972) Isr J Chem 10:765
10. Wolff T, Klaussner B, von Bünau G (1990) Prog Colloid Polym Sci 83:176
11. Wolff T, Klaussner B (1991) J Colloid Interface Sci 145:295
12. Wolff T, Klaussner B, Nees D (1993) Ber Bunsenges Phys Chem 97:1407
13. Mishic JR, Nash RJ, Fisch MR (1990) Langmuir 6:915