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Influence of *trans–cis* photoisomerizations of solubilized compounds on transition temperatures in the system cetyltrimethylammonium bromide–water: light-induced phase transitions

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Transition temperatures (T_{NI}) from the nematic lyotropic liquid-crystalline phase to the isotropic phase were measured for the system cetyltrimethylammonium bromide (CTAB)–water in the presence of small amounts of 3-stilbene carboxylic acid (3SC), 4-stilbene carboxylic acid (4SC) and $\Delta^{2,2'}$-bi-(2*H*-1,4-benzothiazine) (BT). T_{NI} increases as a function of *trans*-3SC or *trans*-4SC concentration, ranging from 0·1 to 0·8 wt %, by up to 12°C. A further increase in T_{NI} between 2 and 5°C can be achieved by photochemically converting the solubilized *trans* stilbene derivatives to the *cis* isomers. Irradiation of a *trans*-3SC containing sample at a temperature just above T_{NI} leads to a light-induced phase transition to the lyotropic liquid-crystalline phase. Solubilization of *trans*-BT causes a slight decrease of T_{NI} while photoisomerization to *cis*-BT increases T_{NI} by 1°C.

1. Introduction

In binary mixtures of cetyltrimethylammonium bromide (CTAB) and water lyotropic liquid-crystalline phases form at CTAB concentrations exceeding 20 per cent by weight. These phases assume a nematic structure between 20 and 25 per cent CTAB [1] in which rod-like aggregates are ordered parallel to a preferred axis, but no long range order perpendicular to this axis exists. Hexagonal, cubic and lamellar structures appear at higher CTAB concentrations [2]. The solubilization of small amounts of certain aromatic compounds in the nematic phase can shift the transition temperatures (T_{NI}) to the isotropic micellar phase in both directions depending on the solubilizate. Since other aromatic compounds do not show this effect, molecular photoreactions converting one class of solubilizates to another allow photochemically triggered phase transitions, provided the sample is irradiated at a temperature between the transition temperatures induced by the photoeduct and by the photoproduct, respectively. This has been demonstrated for the photodimerization of 9-anthracene carboxylic acid [3, 4], the photocyclization of *N*-methyl-*N*-*N*-diphenylamine [5], and for the *cis–trans* photoisomerization of a crown ether bearing azobenzene [6].

In view of possible applications the monomolecular *cis–trans* photoisomerization is most easy to handle, since for bimolecular reactions (such as photodimerizations) slow diffusion of reactants in the highly viscous liquid-crystalline systems is limiting while the photocyclization of diphenylamines requires dissolved oxygen and therefore contact of the sample with air which might cause loss of water by evaporation. We were, therefore, prompted to investigate more photochemical systems capable of *cis–trans* isomerization. For the work presented here we chose 3- and 4-stilbene carboxylic acid

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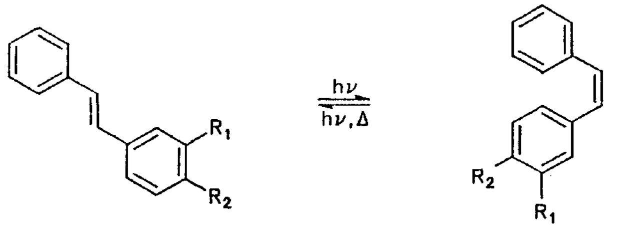
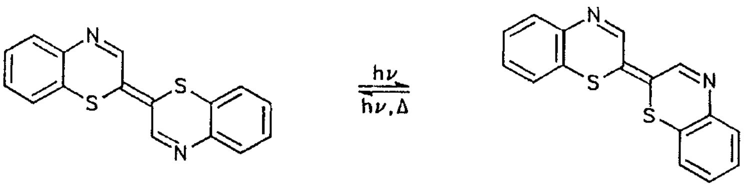
(3SC and 4SC) and $\Delta^{2,2'}$-bi-(2*H*-1,4-benzothiazine) (BT) which photoisomerize according to [7,8]:



trans-3SC, *trans*-4SC *cis*-3SC, *cis*-4SC

(3SC: R_1 = COOH, R_2 = H; 4SC: R_1 = H, R_2 = COOH) (1)



trans-BT *cis*-BT (2)

In all cases the thermodynamically more stable isomer is the *trans* compound, so that a thermal back reaction takes place on a timescale of several days for 3SC and 4SC at room temperature. Moreover, the photoreactions are photo-chemically reversible. The maximum degree of isomerization (reached after exhaustive irradiation: photostationary *cis*/*trans* ratio) depends therefore on the absorption coefficients of the isomers, on quantum yields of *trans–cis* and *cis–trans* isomerizations and on the wavelength to which samples are exposed (cf. [9]).

2. Experimental

2.1. *Materials*

Cetyltrimethylammonium bromide purchased from Merck (p.a. grade) was recrystallized three times from acetone methanol (9 : 1 mixture). 3-stilbene carboxylic acid (3SC) was prepared according to a literature procedure [10, 11] from 3-aminobenzoic acid and 3-phenylacrylic acid; mp194°C (lit. 194–195°C). 4-stilbene carboxylic acid (4SC) was available from a previous investigation [12]. $\Delta^{2,2'}$-bi-(2*H*-1,4-benzothiazine) (BT) was synthesized as described in the literature [13] and recrystallized once from toluene and three times from benzene; mp 286°C (lit. 298–300°C).

2.2. *Solutions*

Samples were prepared in small glass vials by weighing in triply distilled water as well as the chemicals and stirring at 60°C for 5 h after having sealed the vials.

2.3. *Determination of transition temperatures*

Samples inside thermostatted 1 cm cuvettes were placed between two perpendicularly crossed filters for linearly polarized light. The measuring light of an unpolarized He–Ne laser (Polytec) only passes through filters and sample when an

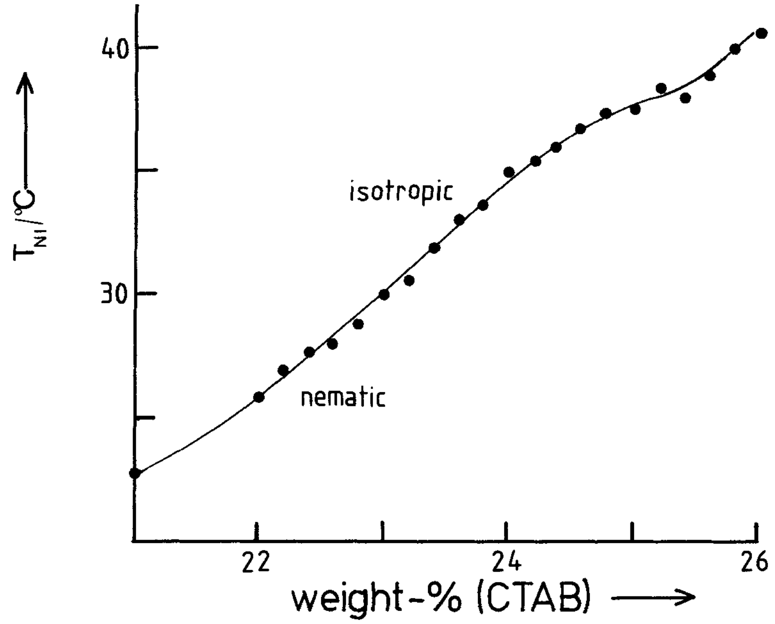


Figure 1. Cut of the phase diagram of the binary system cetyltrimethylammonium bromide (CTAB)-water showing the phase equilibrium line between the lyotropic nematic liquid-crystalline phase and the isotropic micellar phase as detected using linearly polarized light (the two-phase regions could not be resolved). For the complete diagram see [6].

anisotropic (e.g. nematic) phase of the surfactant system rotates the plane of linearly polarized light. Starting in the nematic phase the sample temperature was increased by steps of 0·1°C. The temperatures at which the transparency vanished was taken as the transition temperature to the optically isotropic phase. This procedure was completed within *c*. 5 h.

The T_{NI} data given in figure 1 were obtained employing a computer controlled apparatus which is described elsewhere [6]. In this apparatus the optical path length through the sample was 0·2 cm.

2.4. *Irradiations*

For obtaining the data given in figures 2 and 3 all 3SC and 4SC containing solutions were exposed to the same number of light quanta (i.e. irradiated for 1·5 h) in thermostatted 1 cm cuvettes by a pyrex filtered 100 W high pressure mercury lamp (so that the mercury emission around 313 nm was efficacious for the stilbene derivatives; light of this wavelength is not absorbed by CTAB). The progress of the reaction was followed spectrophotometrically. Exhaustive irradiations were undertaken until constancy of absorption spectra (photostationary *cis*/*trans* ratio). To demonstrate the light-induced phase transition *in situ* (see figure 4) the sample inside the computer controlled apparatus [6] was irradiated through a 2 mm UG 11 filter (Schott) employing a 150 W Xenon lamp as the irradiation source.

To irradiate BT (see data in figure 5) the mercury lamp and an interference filter transmitting at 366 nm were used. Varying the irradiation time between 2 and 5 h did not change the results.

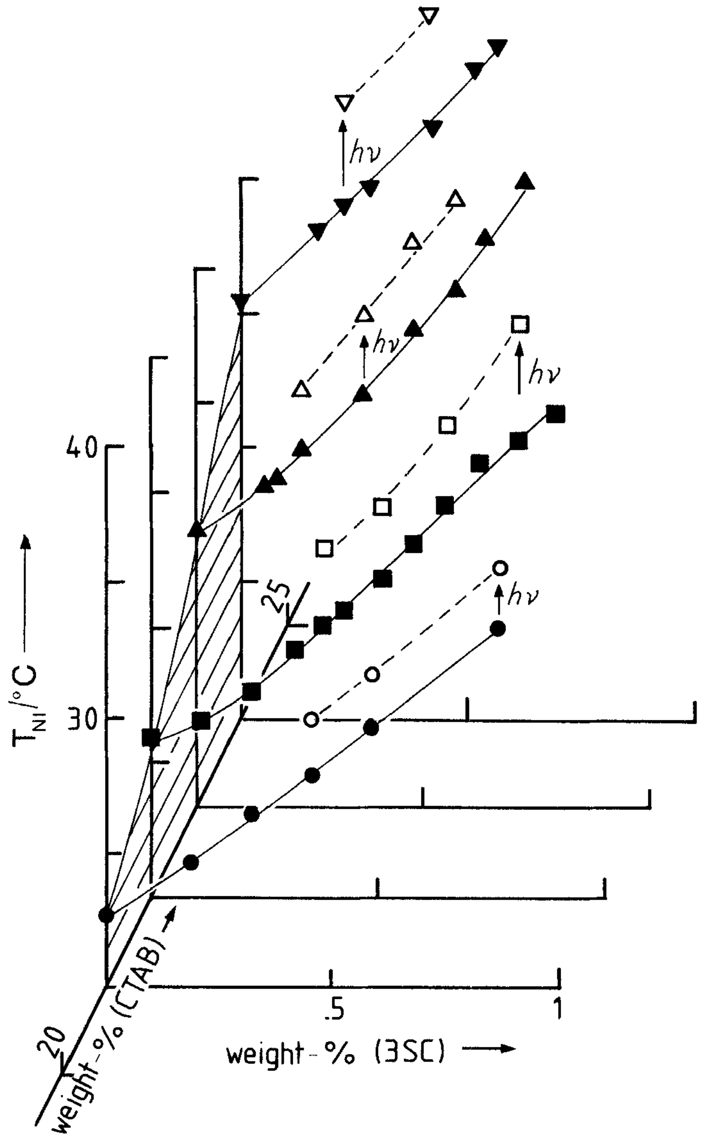


Figure 2. Changes of nematic–isotropic transition temperature T_{NI} as a function of the concentration of added *trans*-3-stilbene carboxylic acid (3SC; filled symbols) for 21 per cent CTAB (●), 22 per cent CTAB [■], 23 per cent CTAB (▲), and 24 per cent CTAB (▼). T_{NI} variations upon photoisomerization of *trans*-3SC to *cis*-3SC are indicated by the arrows denoted *hν*. Open symbols refer to values obtained after 1·5 h irradiation. The hatched area in the T_{NI} versus per cent CTAB plane represents the nematic phase.

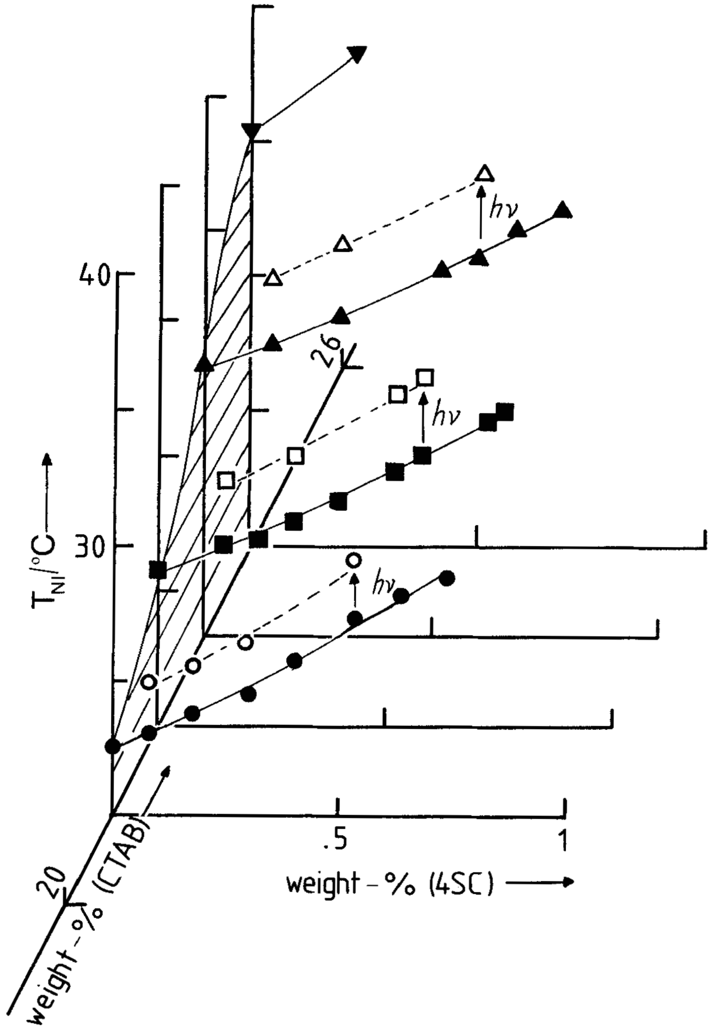


Figure 3. Changes of nematic–isotropic transition temperature T_{NI} as a function of the concentration of added *trans*-4-stilbene carboxylic acid (4SC; filled symbols) for 21 per cent CTAB (●), 22 per cent CTAB (■), 23 per cent CTAB (▲), and 24 per cent CTAB (▼). T_{NI} variations upon photoisomerization of *trans*-4SC to *cis*-4SC are indicated by the arrows denoted *hν*. Open symbols refer to values obtained after 1·5 h irradiation. The hatched area in the T_{NI} versus per cent CTAB plane represents the nematic phase.

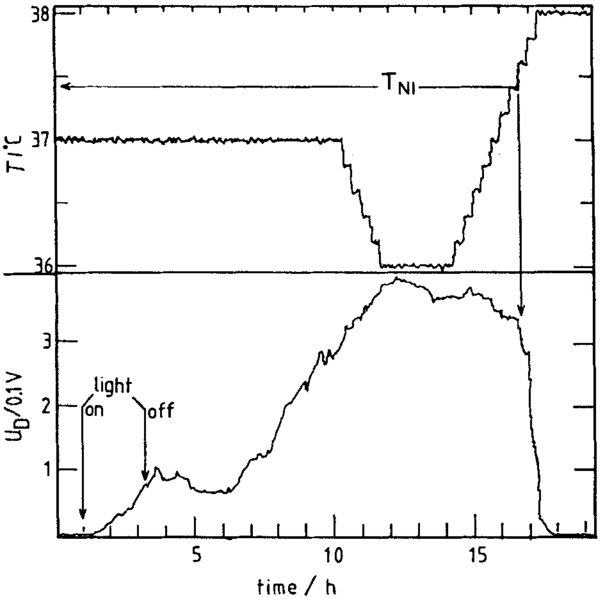


Figure 4. Light-induced phase transition in the CTAB-H_2O system containing 23 per cent CTAB and 0·4 per cent 3SC by weight. Bottom part: photodiode voltage U_D measured with a He–Ne laser light passing through the sample placed between crossed filters for linearly polarized light as a function of time. Between the marks light on/off the sample is irradiated by light absorbed by 3SC. Upper part: sample temperature as a function of time throughout the experiment.

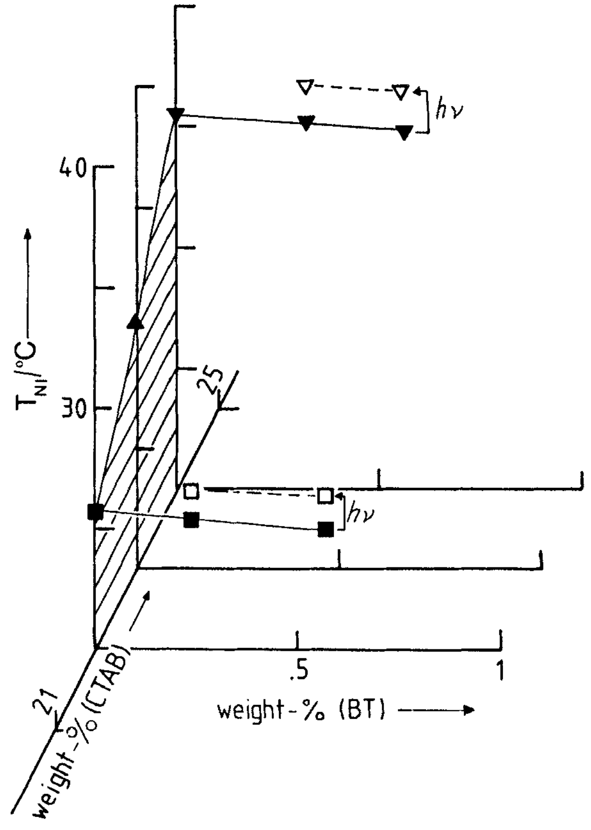


Figure 5. Changes of nematic–phase transition temperature T_{NI} as a function of the concentration of added $\Delta^{2,2'}$-bi-(2*H*-1,4-benzothiazine) (BT; filled symbols) for 22 per cent CTAB (■) and 24 per cent CTAB (▼). T_{NI} variations upon photoisomerization of *trans*-BT to *cis*-BT are indicated by the arrows denoted *hν*. Open symbols refer to values obtained after 1·5 h irradiation at 366 nm. The hatched area in the T_{NI} versus per cent

2.5. *Thermal reisomerization*

To determine the rate constant of the thermal reisomerization from *cis*-4SC to *trans*-4SC a solution containing 0·06 mol/dm^3 of CTAB and 0·004 mol/dm^3 of *cis*-4SC was used. This concentration corresponds to the 21 per cent CTAB/0·85 per cent 4SC mixture which had to be diluted by a factor of 10 in order to allow direct observation of absorption changes on the UV spectrophotometer using thermostatted 0·01 cm cuvettes (Hellma). The solution was irradiated until constancy of absorption spectrum and the reisomerization was followed by monitoring the growth in the absorption (A) at 315 nm. The rate constant k is the slope of a plot of $\ln(A\infty - A)$ versus time ($A\infty$ is the absorption after infinite time).

3. Results

Figure 1 shows the phase equilibrium line between the nematic and the isotropic phase in the CTAB-H_2O system. The measured points represent transitions to the isotropic phase, i.e. the upper border of a two phase region which cannot be distinguished from the nematic phase by our apparatus. In figure 2 experiments with 3-stilbene carboxylic acid (3SC) are collated. When small amounts (up to 0·8 per cent by weight corresponding to $3\cdot5 \times 10^{-2}$ mol/kg) of *trans*-3SC are solubilized in the nematic phase (at between 21 and 24 per cent CTAB, i.e. between 0·57 and 0·66 mol/kg) the transition temperature increases with the concentration of 3SC. A further T_{NI} increase is observed after irradiation with light absorbed by the solubilizate only, i.e. after photoconverting *trans*-3SC to *cis*-3SC. The photostationary concentration ratio of *cis* and *trans* isomers after exhaustive irradiation can be estimated from absorption spectra (as described in [12]) to contain at least 80 per cent compound. However, this must be considered an upper limit under our conditions since (i) the irradiation time was kept constant (1·5 h) irrespective of the solubilizate concentration, (ii) the solutions were not stirred during the irradiations, and (iii) at 313 nm light cannot penetrate more than a few μm into the sample due to absorption coefficients [14]. Thus, in the highly viscous nematic systems slow diffusion of solubilizate molecules (required to exchange material near the irradiated surface) limits the degree of photochemical conversion. Therefore, the lowest degree of photoconversion can be expected in the solutions most concentrated in solubilizate. Spot checks (of samples whose absorption spectra were measured after irradiation, T_{NI} determination procedure and dilution) indicated photochemical *trans–cis* conversions of 25 through 60 per cent. As compared to air saturated solutions no significant change of the results was obtained when the irradiations were performed under a nitrogen atmosphere. Figure 3 illustrates results using 4SC containing solutions which behave similarly to 3SC solutions. A comparison of figures 2 and 3 reveals that changes in T_{NI} upon solubilizing the *trans* compounds as well as upon irradiation exhibit larger amplitudes for 3SC.

This prompted us to choose a sample containing 23 per cent CTAB and 0·4 per cent of *trans*-3SC ($T_{NI} = 36{\cdot}6°C$) to demonstrate the light-induced phase transition *in situ* as illustrated in figure 4. In the bottom part of the figure a photodiode voltage (U_D) is recorded as a function of time. The photodiode measures the light intensity of a He–Ne laser passing through the sample placed between two perpendicularly crossed filters for linearly polarized light [6]. Therefore, a photodiode signal is only observed when the optically anisotropic nematic phase is present. The upper part of the figure displays the sample temperature during the experiment. It follows from inspection of the figure that at the beginning of the experiment $U_D = 0$ at 37°C proving the sample to be isotropic. After one hour at this temperature an irradiation for *c.* 2 h was started while the temperature was kept at 37°C. After 0·5 h of irradiation U_D increased indicating the photochemically induced formation of the nematic phase. After switching off the light the sample stayed nematic, some variation of U_D, however, was observed which might be caused by slow diffusion of the irradiation product (*cis*-3SC, inhomogeneously concentrated after irradiation, cf. [14]) from the irradiated surface into the solution. After 10 h at 37°C a temperature program for a computer controlled T_{NI} determination (cf. [6]) was started which yielded T_{NI} 37·4°C for the irradiated sample.

In both the stilbene derivatives the photoisomerization is reversible either photochemically (by exposure to light of a lower wavelength absorbed predominantly by the *cis* isomer) or thermally (by storing the sample for a few days in the dark at an elevated temperature). In this way T_{NI} can be shifted in both directions several times. The T_{NI} difference between a *trans* isomer containing sample and the corresponding irradiated one narrowed with the number of reisomerizations (4SC allowed for more cycles than 3SC) indicating that side reactions consume the stilbenes. These side reactions were not investigated in our systems. They are, however, likely to be the formation of phenanthrene derivatives [15, 16]. Also, owing to high local concentrations of *trans*-stilbenes photodimerization may take place [17]. The thermal *cis*–*trans* reisomerization of 4SC proceeded with a rate constant k of $6{\cdot}5 \times 10^{-6}\,s^{-1}$ at 70°C in 0·06 M CTAB to be compared with $2 \times 10^{-6}\,s^{-1}$ in 0·25 M CTAB at 60°C [12]. It can be estimated from these data that less than 2 per cent of the *cis* molecules can react thermally to give the *trans* form during the T_{NI} determinations performed at 30–40°C.

Much smaller effects on T_{NI} were found upon solubilizing $\Delta^{2,2'}$-bi-(2*H*-1,4-benzothiazine) (BT) and upon irradiation (see figure 5). In contrast to the stilbene derivatives T_{NI} is reduced in the presence of *trans*-BT. The behaviour of the systems described is, however, similar in that the photoconversion to *cis*-BT has a T_{NI} increasing effect.

4. Discussion

The T_{NI} versus solubilizate concentration curves in figures 2 and 3 for corresponding irradiated and non-irradiated samples appear parallel. This is a consequence of the decreasing concentration ratios of *cis* and *trans* stilbene compounds present (due to the experimental conditions) after irradiation of samples with increasing solubilizate concentration. If each sample was exhaustively irradiated under stirring, a steady increase of T_{NI} differences between irradiated and non-irradiated samples with increasing solubilizate concentration could be expected as found for *N*-methyl-*N*-, *N*-diphenylamine containing systems [5].

The small T_{NI} changes obtained upon irradiation of BT led us not to investigate this system in detail. However, as the rate of thermal back reaction seems to depend strongly on the solvent [8, 13], the concentration ratio *cis*-BT: *trans*-BT may diminish while the T_{NI} determination proceeds. Therefore a T_{NI} determination performed under steady irradiation might give different results.

At the present stage of the investigations the molecular interactions responsible for the observed effects are not yet obvious. Spectroscopic examinations such as ^{1}H NMR measurements [18] are planned which might give information about the size and shape of the micelles. A common feature of the present observations is that T_{NI} in the presence of the *cis* isomers always exceeds T_{NI} of the systems containing the *trans* compounds only. This behaviour is also similar to the observations obtained using a crown ether bearing azobenzene (AB15C5) as a solubilizate [6]. One reason for this might be that the longish *trans* isomers induce a packing of CTAB micelles which favours the flexibility of rod-like aggregates thus stabilizing the isotropic phase (cf. [19]). For BT and AB15C5 this effect leads to a decrease of T_{NI} not only to samples containing the respective *cis* isomers but also compared to the pure CTAB-H_2O systems. In this respect BT and AB15C5 differ from 3SC and 4SC which cause T_{NI} to rise (as compared to pure CTAB-H_2O) even in the *trans* form. Here a partial dissociation of the aromatic acids may play a role: although only a few percent of the stilbene carboxylic acid molecules are dissociated in micellar CTAB solutions [12], the electrolyte generated in this way can affect the size and shape of the micelles and the degree of counterion dissociation. It may, thus, influence the phase transition process.

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