

## LIGHT-INDUCED VISCOSITY CHANGES OF AQUEOUS SOLUTIONS CONTAINING 9-SUBSTITUTED ANTHRACENES SOLUBILIZED IN CETYLTRIMETHYLAMMONIUM MICELLES

NORBERT MÜLLER, THOMAS WOLFF and GÜNTHER VON BÜNAU

*Physikalische Chemie, Universität Siegen, D-5900 Siegen 21 (F.R.G.)*

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### Summary

Micellar solutions of various 9-substituted anthracenes show rheopectic, thixotropic and viscoelastic behaviour depending on composition. Large viscosity changes are induced by the small changes in solubilizate concentration caused by photodimerization of the anthracenes at wavelengths exceeding 300 nm. Photocleavage of the dimers at lower wavelengths allows viscosity modulation by suitable choice of irradiation conditions.

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### 1. Introduction

9-substituted anthracenes are known to form dimers on irradiation at  $\lambda > 300$  nm [1, 2] which can be split thermally and photochemically (at  $\lambda < 300$  nm) to re-form the monomers [3]. In previous studies [4, 5] we have shown that dimerization quantum yields and ratios of isomeric dimerization products depend on the solvent and are particularly sensitive to micro-environments such as those existing in aqueous micellar solutions. It has been noted that the viscosity of aqueous solutions of some 9-substituted anthracenes solubilized in cetyltrimethylammonium bromide (CTAB) micelles is strongly dependent on the concentration of the anthracenes.

Other groups had studied the viscosities of micellar solutions earlier [6 - 14], and had paid special attention to the viscoelastic properties of some of these systems. Even dilute aqueous micellar solutions ( $2 \times 10^{-4}$  M [10]) were found to exhibit viscoelasticity. The systems investigated contained micelles, usually cetyltrimethylammonium micelles, with added KBr and large organic counter-ions or large organic molecules were solubilized within the micellar phase. Since anthracenes, their 9-substituted derivatives and their photodimers belong to the latter categories, a somewhat closer inspection of the flow properties of their micellar solutions was indicated. We describe here the rheological behaviour of these solutions and the special photochemical effects on the non-newtonian flow phenomena.

## 2. Experimental details

### 2.1. Materials

Anthracene (Fluka; minimum purity, 99%), CTAB (Merck, pro Analyse), 9-chloromethylantracene (Ega; purity, 97%), 9-anthracenecarbaldehyde (Ega; purity, 97%), 9-anthracenecarboxylic acid (Ega; purity, 98% - 99%), 9-acetylanthracene (Ega; purity, 95%), 9-anthracenecarbonitrile (Ega; purity, 97%), 9-phenylantracene (Ega; purity, 99%), 9-methylantracene (Ega; purity, 98%), 9-( $\omega$ -nitrovinyl)anthracene (Ega; purity, 98%) and (+)-1-(9-anthryl)-2,2,2-trifluoroethanol (Ega; purity, 98%) were used as received. Cetyltrimethylammonium chloride (CTAC), 9,10-dimethylantracene and 9-hydroxymethylantracene were available from previous investigations [4, 15].

### 2.2. Measurements

Micellar solutions were prepared as described elsewhere [15]. The dynamic viscosities of non-viscoelastic solutions were measured at  $25.2 \pm 0.2$  °C using Ostwald viscometers. The values were reproducible to within 2% [16]. The viscosities of the viscoelastic samples were measured using a Haake Rotovisco RV 100/CV 100 rotational viscometer equipped with standard cylindrical and Mooney-Ewart measuring arrangements.

Irradiations at  $\lambda > 300$  nm were performed at ambient temperature in 1 cm  $\times$  1 cm cuvettes using a Philips HPK 125 high pressure mercury lamp and a Pyrex filter. The irradiation time was 5 min. Irradiations at  $\lambda = 249$  nm were carried out using 1000 pulses of the KrF line of a Lambda Physik EMG 500 excimer laser.

The absorption spectra were measured using a Beckman Acta M VII spectral photometer, the fluorescence spectra were measured using a Spex Fluorolog spectral fluorometer and the pH values were measured using a Philips PW 9414 ion activity meter.

## 3. Results

Qualitative solubilization data for a variety of anthracene derivatives in aqueous micellar solutions and the flow behaviour of the solutions are given in Table 1. In these experiments viscoelasticity was detected by visual observation of a swirled solution [17]. Accurate measurements may therefore reveal small viscoelastic effects in some of the other solutions.

Dynamic viscosities were measured for various aqueous solutions containing CTAB and 9-methylantracene. Viscoelasticity was not observed in these solutions. The results are summarized in Table 2 and show that the viscosity of pure aqueous CTAB solutions is almost independent of the concentration within the range investigated. A significant increase in the viscosity was observed, however, when 9-methylantracene was added to these micellar solutions [7, 9]. As shown in Table 2 the viscosity of a CTAB

TABLE 1

Qualitative solubility and flow behaviour of aqueous micellar solutions of anthracene derivatives

<i>Solute</i> <sup>a</sup>	<i>Solubility</i>	<i>Enhancement of viscosity</i>	<i>Viscoelasticity</i>
Anthracene	Moderate	No	No
9,10-dimethylantracene	Poor	No	No
9-phenylantracene	Poor	No	No
9-anthracenecarbaldehyde	Poor	No	No
9-anthracenecarbonitrile	Poor	No	No
9-( $\omega$ -nitrovinyl)anthracene	Poor	No	No
9-hydroxymethylantracene	Almost complete	Moderate	No
9-acetylantracene	Almost complete	Strong	No
9-chloromethylantracene	Almost complete	Strong	No
9-methylantracene	Complete	Strong	No
9-anthracenecarboxylic acid	Complete	Strong	Yes
(+)-1-(9-anthryl)-2,2,2-trifluoroethanol	Complete	Strong	Yes

<sup>a</sup>In each case 0.1 g of solute was mixed with 10 ml of a 0.25 M cetyltrimethylammonium solution.

TABLE 2

Viscosity at 25.2 °C of aqueous solutions containing various concentrations of cetyltrimethylammonium bromide and 9-methylantracene

<i>Concentration (mmol l<sup>-1</sup>)</i>		<i>Viscosity (mPa s)</i>	
<i>CTAB</i>	<i>9-methylantracene</i>	<i>Before irradiation at <math>\lambda &gt; 300</math> nm</i>	<i>After irradiation at <math>\lambda &gt; 300</math> nm</i>
50		1.03	
100		1.16	
150		1.30	
200		1.48	
250		1.71	
125	13.0	1.39	
	26.0	2.38	
	39.0	4.11	
250	13.2	2.79	2.16
	26.1	7.15	4.38
	31.7	13.0	
	39.1	27.5	10.1
	41.6	35.1	
	46.9	105	
	52.1	413	191

solution of concentration 0.25 M increased by a factor of about 150 when the 9-methylanthracene concentration was raised by only about a factor of 4. Irradiation of these solutions, which are known to yield photodimers, leads to a substantial reduction in the viscosity when only a small fraction of the monomers is converted. Dimers evidently have much less effect than monomers on the viscosity. It must be remembered that the irradiation time was kept constant (5 min) and that photodimerization can only occur when a micelle contains at least two monomer molecules. The degree of conversion must therefore increase with increasing monomer concentration. However, it also depends on optical density.

No significant viscosity changes were observed when analogous experiments using the anthracene solute were performed (Table 3). In addition, when the surfactant was changed from CTAB to CTAC, which differ only in the kind of counter-ions present, only a slight enhancement of viscosity was observed on addition of 9-methylanthracene (see Tables 2 and 3).

The results of experiments with 9-anthracenecarboxylic acid as a solute in CTAB solutions (Table 4) are qualitatively similar to those with 9-methylanthracene. The viscosity enhancement with increasing concentration of solubilizate was even larger. These measurements were performed only in concentration ranges in which viscoelasticity was not observed. On irradiation at  $\lambda > 300$  nm photodimers are formed which reduce the viscosity. When an irradiated solution was reirradiated at  $\lambda = 249$  nm (light of this wavelength is absorbed by the dimers and in part by the monomers), the viscosity increased again indicating some back reaction (see Table 4).

The pH value of an aqueous solution containing 0.25 M CTAB and 0.002 M anthracenecarboxylic acid was found to be 3.1 whereas a corresponding solution without the acid showed a pH of 6.5. It can be estimated that at least half of the anthracenecarboxylic acid molecules are dissociated in CTAB solution. This is in accordance with the absorption and fluorescence

TABLE 3

Viscosity at 25.2 °C of aqueous solutions containing 0.25 M of either cetyltrimethylammonium bromide or cetyltrimethylammonium chloride and various concentrations of 9-methylanthracene or anthracene

<i>Micellar solution</i>	<i>Concentration (mmol l<sup>-1</sup>)</i>		<i>Viscosity (mPa s)</i>
	<i>9-methylanthracene</i>	<i>Anthracene</i>	
CTAC			1.60
	13.2		1.64
	26.0		1.70
	39.4		1.75
	44.2		1.78
CTAB		14.0	2.16
		28.1	2.13

TABLE 4

Viscosity at 25.2 °C of aqueous solutions containing 0.25 M cetyltrimethylammonium bromide and various concentrations of 9-anthracenecarboxylic acid

Concentration of 9-anthracene- carboxylic acid (mmol l <sup>-1</sup> )	Viscosity (mPa s)		
	Before irradiation at $\lambda > 300$ nm	After irradiation at $\lambda > 300$ nm	After reirradiation at $\lambda = 249$ nm
11.3	3.59		
22.5	9.49	7.41	7.93
24.8	12.8		
27.0	18.9		
33.8	89.5		
36.0	110		
27.0	18.9	17.2	

spectra of such solutions which differ for the anion and the undissociated acid [18].

Viscoelastic properties were observed when the concentration ratio of 9-anthracenecarboxylic acid to the surfactant was increased. This was done by either increasing the solute concentration or decreasing the surfactant concentration beyond the range covered by Tables 2 and 4.

Two viscoelastic solutions (A, 0.25 M CTAB and 0.0675 M anthracenecarboxylic acid; B, 0.005 M CTAB and 0.0036 M anthracenecarboxylic acid) were tested using the rotational viscometer. Both solutions could only be measured at low velocity gradients (about 3 s<sup>-1</sup>). Otherwise the structures of the solutions appeared to be changed.

The flow curve of solution A at 25.5 °C showed a strongly thixotropic behaviour [19] which was suppressed at 40 °C (*cf.* ref. 20). Evaluation of the data obtained from oscillating shear experiments gave a complex viscosity  $\eta^* = \eta' + i\eta''$  represented by an imaginary part  $\eta''$  and a real part  $\eta'$  where  $\eta'$  refers to the viscous contribution to the viscosity and  $\eta''$  to the elastic contribution to the viscosity [21]. The viscous and elastic contributions of solution A were found to be almost equal at the beginning of the shear, but the elastic part diminished with the shear time. Interestingly, a solution composed as solution B using CTAC instead of CTAB was also viscoelastic.

Rheoplectic behaviour [19] was derived from the flow curve of solution B at 25.5 °C (see refs. 9 and 22). The solution also showed rheopexy at 40 °C at a reduced value of the viscosity. The viscous contribution to the complex viscosity exceeded the elastic contribution; both increased with shear time, the elastic contribution more strongly than the viscous contribution.

#### 4. Discussion

The viscosity of pure aqueous solutions of CTAB depends on the concentration as reported by Ekwall *et al.* [23]. These workers obtained a concentration range above the critical micelle concentration in which the

viscosity was proportional to the CTAB concentration until at  $c_{\text{CTAB}} \geq 0.3$  M the viscosity increased more rapidly. This was explained by the formation of rod-like micelles at the expense of spherical micelles. Previous studies of viscoelastic effects have also shown that rod-like micelles must be present in viscoelastic solutions [13, 14]. Therefore a probable cause of the viscosity increase observed on addition of some 9-substituted anthracenes to CTAB solutions is the formation of rods induced by the incorporation of anthracenes at CTAB concentrations below 0.3 M.

The ability to enhance viscosity, *i.e.* to induce rod formation, appears to depend on specific steric interactions between the surfactant and the solubilize molecules. Viscosity effects are observed in CTAB solutions of 9-methylanthracene but not of anthracene, 9,10-dimethylanthracene and other poorly soluble anthracene derivatives (see Table 1). The photodimers of 9-methylanthracene probably belong to the latter group.

The effect also appears to depend on the extent of the ionic interactions in the diffuse double layer surrounding the micelle. Viscoelasticity is not observed in CTAC solutions containing solubilized 9-methylanthracene which is consistent with the lack of rod formation in pure CTAC solutions [24]. In contrast, the 9-anthracenecarboxylate anion investigated here induces rod formation even in CTAC solutions. This corresponds to the analogous effect shown by substituted benzoates and naphthoates [6, 7, 10, 11, 13, 14].

The photochemically induced viscosity changes in these solutions indicate a marked dependence on the concentration of 9-methylanthracene and anthracenecarboxylate anions. These solubilizates can be removed by photodimerization and regained by splitting the dimers. It should be possible to attain photostationary concentrations of monomers and dimers and to modulate the viscosity of these solutions simply by exposure to a suitable radiation field.

## 5. Conclusion

A variety of viscosity effects including elasticity, thixotropy and rheopexy were obtained in aqueous solutions containing cetyltrimethylammonium micelles and 9-substituted anthracenes. Rheological effects have been observed in surfactant solutions for the first time: the viscosity of solutions of 9-methylanthracene and of 9-anthracenecarboxylic acid can be decreased by irradiation at  $\lambda > 300$  nm. The viscosity can be increased again by reirradiation at  $\lambda = 249$  nm.

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