

TIME STABILITY OF DETERGENT (MICELLE) SYSTEMS CONTAINING ORGANIC DYES

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Micelle systems containing organic dyes are often used as *in vitro* models to study physical processes of photosynthesis. Time stability is an important characteristic of the applicability of this model. In this paper the dependence of optical properties of dye-detergent systems on the duration of keeping the system in dark is investigated. It can be stated on the basis of our measurements that the dye systems studied, kept in the dark for a longer period, especially below critical micelle concentration (c.m.c.) and at higher temperatures, fade and seem to become "exhausted", *i.e.* their absorption maxima and fluorescence intensities decrease.

Introduction

Micelle systems containing organic dyes are often used as *in vitro* models of chloroplasts, as they approximate well the structure of chloroplasts well [1—3], which play an important role in photosynthesis. The model system being exposed to various external influences during the investigation, its stability against these influences is at the same time a measure of its applicability.

The temperature dependence of the stability of micelle systems has been investigated earlier [4]. The present paper describes the influence on stability exerted by holding the system in dark for a longer period.

Composition of the systems. Experimental methods

The composition of the model used was the same as described earlier [4]. Absorption and emission properties of three dye-detergent systems, namely thionin + sodium laurylsulphate (Th + SLS); Rhodamine 6G + sodium laurylsulphate (Rh 6G + SLS); methylene blue + sodium laurylsulphate (MB + SLS) were studied at three different temperatures (30 °C, 50 °C, 70 °C), holding the systems in the dark. Absorption and emission spectra were measured at the time of preparation of the solutions as well as 6, 24, 54, and 96 hours later. This choice of the times of measurement was determined partly by the circumstance that we wished to follow the changes in the spectral characteristics after different times spent in the dark, and partly by practical (technical) conditions of the measurements.

Darkness and constant temperature were secured by placing the systems examined in a light-tight thermostat.

A recording spectrophotometer Optica Milano Type CF 4 DR was applied for absorption measurements, a recording spectrophotometer Type DFS—12 for measuring the emission. During the measurements the temperature was held constant by cuvette holders the temperature of which was regulated by a Höppler thermostat Type U—10.

Results and discussion

1. Absorption measurements

The degree of stability of the micelle system clearly depends on the changes in the absorption properties of the system produced by holding it in the dark at constant temperature for different times.

The dependence of the micelle system on these parameters is presented in Table I for the α absorption band of thionin. It can be seen that above c.m.c. the sys-

Table I
Values and location of $k(\lambda)_{\max}$ of the α absorption band of Th + SLS systems

t (°C)	T (hours)		$C_{SLS} \cdot 10^3$ (M/l)					
			0	2	3	3.5	4	8
30	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.610	0.126	0.324	0.594	0.670	0.706
		λ_{\max} (nm)	600.0	601.0	603.0	603.5	602.0	603.5
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.592	0.104	0.240	0.407	0.648	0.731
		λ_{\max} (nm)	600.0	604.0	602.0	603.0	603.0	603.0
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.611	0.101	0.214	0.329	0.616	0.706
		λ_{\max} (nm)	600.5	600.0	603.0	603.0	603.5	603.5
50	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.564	0.155	0.348	0.581	0.645	0.695
		λ_{\max} (nm)	598.0	602.5	601.0	601.5	601.0	601.0
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.559	0.123	0.281	0.421	0.625	0.695
		λ_{\max} (nm)	597.5	600.0	601.0	600.5	601.0	601.5
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.537	0.125	0.260	0.366	0.614	0.692
		λ_{\max} (nm)	597.0	599.0	600.5	601.0	601.0	601.0
70	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.596	0.208	0.415	0.527	0.583	0.685
		λ_{\max} (nm)	597.0	602.0	601.0	601.0	601.5	600.5
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.575	0.197	0.330	0.434	0.523	0.673
		λ_{\max} (nm)	595.5	598.0	598.0	600.0	600.5	600.5
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.492	0.178	0.283	0.373	0.489	0.636
		λ_{\max} (nm)	595.5	598.0	600.0	601.0	600.5	600.5

tem Th+SLS is very stable, even after a longer period (96 hours) in the dark. At low detergent concentrations, however, the maxima of the α -band significantly decrease with increasing duration of the dark period, even at lower temperatures. At 70 °C, even systems found to be stable above c.m.c. do not show such stability; at this temperature an important decrease in absorption is found even at higher detergent concentrations. It can also be seen that at low detergent concentrations, especially at 50 °C and 70 °C, the maximum of the α -band is slightly shifted towards shorter wavelengths; above c.m.c. this shift cannot be observed.

Table II

Values and location of $k(\lambda)_{\max}$ of the α absorption band of Rh 6G+SLS systems

t (C°)	T (hours)		$C_{SLS} \cdot 10^3 (M/l)$					
			0	2	3	3,5	4	8
30	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.789	0.764	0.850	0.880	0.895	0.940
		λ_{\max} (nm)	528.0	536.5	535.5	535.5	535.5	535.0
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.916	0.735	0.828	0.875	0.885	0.920
		λ_{\max} (nm)	527.5	535.5	535.0	535.0	535.0	535.0
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.843	0.738	0.836	0.862	0.886	0.892
		λ_{\max} (nm)	526.0	534.0	535.0	535.0	535.0	535.0
50	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.840	0.800	0.845	0.851	0.849	0.850
		λ_{\max} (nm)	526.0	534.0	534.0	534.0	534.0	534.0
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.811	0.776	0.835	0.854	0.860	0.890
		λ_{\max} (nm)	526.5	535.0	534.5	534.0	534.0	533.5
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.855	0.756	0.830	0.850	0.856	0.897
		λ_{\max} (nm)	526.5	534.5	535.0	535.0	534.5	533.5
70	0	$k(\lambda)_{\max}$ (cm ⁻¹)	0.819	0.767	0.794	0.822	0.826	0.844
		λ_{\max} (nm)	527.0	534.5	534.0	534.0	534.0	534.0
	24	$k(\lambda)_{\max}$ (cm ⁻¹)	0.806	0.735	0.765	0.810	0.803	0.860
		λ_{\max} (nm)	526.5	534.5	534.5	534.5	534.5	534.0
	96	$k(\lambda)_{\max}$ (cm ⁻¹)	0.815	0.721	0.797	0.819	0.812	0.867
		λ_{\max} (nm)	526.0	534.0	533.0	533.5	533.5	532.0

Table II shows the changes in the absorption maxima of the system Rh 6G+SLS, caused by holding the system in the dark. It can be seen that the influence of the dark period on the absorption of the system is less important, the changes remain generally below 5%; at higher temperatures, the changes are somewhat more significant.

Concerning the changes in absorption of MB+SLS systems due to longer periods in the dark, the same can be said as for Th+SLS systems.

2. Emission measurements

The changes in emission caused by longer dark periods are presented in Table III. It can be seen that, up to $4 \cdot 10^{-3}$ M/l SLS concentration, the luminescence intensity at 30 °C decreases due to the dark period, while at higher concentrations it remains constant. At 50 °C and 70 °C a significant decrease in intensity is observed even at

Table III

Values and location of emission maxima ($f_q(\lambda)_{\max}$) of Th+SLS systems

t (°C)	T (hours)		$C_{SLS} \cdot 10^3$ (M/l)					
			0	2	3	3.5	4	8
30	0	$f_q(\lambda)_{\max}$ (%)	100.0	17.3	42.3	76.4	146.4	179.0
		λ_{\max} (nm)	619.0	618.5	621.5	621.0	621.0	620.5
	24	$f_q(\lambda)_{\max}$ (%)	104.0	11.3	29.9	50.5	137.4	184.3
		λ_{\max} (nm)	620.0	621.5	620.0	622.0	621.0	620.5
	96	$f_q(\lambda)_{\max}$ (%)	76.2	9.6	24.8	40.5	133.3	179.8
		λ_{\max} (nm)	619.0	621.5	622.5	621.0	620.	620.0
50	0	$f_q(\lambda)_{\max}$ (%)	100.0	32.0	42.6	73.2	121.3	166.7
		λ_{\max} (nm)	620.0	621.5	621.0	620.5	619.5	620.0
	24	$f_q(\lambda)_{\max}$ (%)	98.5	26.3	43.2	59.3	103.5	151.7
		λ_{\max} (nm)	620.0	621.5	621.0	620.5	620.0	620.0
	96	$f_q(\lambda)_{\max}$ (%)	90.9	12.6	32.9	46.7	69.4	104.7
		λ_{\max} (nm)	620.0	621.5	622.0	621.5	620.5	620.5
70	0	λ_{\max} (nm)	100.0	53.9	62.6	71.2	81.8	143.6
		$f_q(\lambda)_{\max}$ (%)	619.0	622.0	621.5	620.5	620.0	619.5
	24	λ_{\max} (nm)	93.2	49.4	55.0	64.5	69.8	137.6
		$f_q(\lambda)_{\max}$ (%)	619.5	621.5	621.5	621.0	620.0	619.5
	96	$f_q(\lambda)_{\max}$ (%)	95.6	41.4	49.1	57.0	71.8	133.4
		λ_{\max} (nm)	620.0	622.0	621.0	621.5	620.5	620.0

higher detergent concentrations. This shows that the systems seem to become "exhausted", especially at higher temperatures.

Table IV shows the changes caused by the dark period in fluorescence intensity of the Rh 6G+SLS systems. It can be seen that at detergent concentrations below c.m.c. the values of $f_q(\lambda)_{\max}$ significantly decrease at all three temperatures; above c.m.c. a less significant increase is found.

Concerning the changes in fluorescence intensity due to the dark period of systems containing MB, the same can be said as in the case of thionin.

Table IV

 Values and location of emission maxima ($f_q(\lambda)_{\max}$) of Rh 6G+SLS systems

t (°C)	T (hours)		$C_{\text{SLS}} \cdot 10^3$ (M/l)					
			1	2	3	3,5	4	8
30	0	$f_q(\lambda)_{\max}$ (%)	100.0	21.2	71.5	82.1	84.8	81.9
		λ_{\max} (nm)	552.0	558.5	559.0	559.5	559.0	557.0
	24	$f_q(\lambda)_{\max}$ (%)	101.5	7.5	48.0	79.2	85.4	73.6
		λ_{\max} (nm)	553.0	558.5	561.0	561.0	560.0	558.5
	96	$f_q(\lambda)_{\max}$ (%)	124.6	6.9	43.2	87.1	101.9	93.8
		λ_{\max} (nm)	553.0	557.5	560.5	559.5	559.0	557.5
50	0	$f_q(\lambda)_{\max}$ (%)	100.0	29.3	56.6	66.5	75.4	74.3
		λ_{\max} (nm)	552.5	561.0	560.5	560.0	559.0	558.0
	24	$f_q(\lambda)_{\max}$ (%)	104.8	24.7	53.8	71.8	80.0	64.6
		λ_{\max} (nm)	553.0	560.0	560.5	560.0	558.5	557.0
	96	$f_q(\lambda)_{\max}$ (%)	104.4	13.1	44.4	58.5	71.0	71.4
		λ_{\max} (nm)	553.0	560.5	559.5	559.5	558.5	558.0
70	0	$f_q(\lambda)_{\max}$ (%)	100.0	16.3	35.9	45.9	61.3	74.4
		λ_{\max} (nm)	553.5	555.0	559.5	559.5	558.0	557.0
	24	$f_q(\lambda)_{\max}$ (%)	111.7	16.2	35.7	56.3	61.9	95.2
		λ_{\max} (nm)	554.0	557.5	561.0	560.0	560.0	557.5
	96	$f_q(\lambda)_{\max}$ (%)	103.2	11.5	39.8	49.2	56.7	83.8
		λ_{\max} (nm)	554.0	558.5	560.0	560.0	559.5	556.0

Summarizing the results, it can be stated that below c.m.c. the systems studied significantly fade by being kept in the dark. Good stability above c.m.c. is found in Rh 6G+SLS systems. In Th+SLS and MB+SLS systems above c.m.c., slight decreases in absorptions intensity can be observed at higher temperatures. The systems seem to become "exhausted" by the dark period, their ability of emission decreases.

Below c.m.c., *i.e.* before the formation of an ordered structure, the three dye-detergent systems studied are instable, while above c.m.c. they are more stable at all temperatures.

References

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ЗАВИСИМОСТЬ СТАБИЛЬНОСТИ СИСТЕМ КРАСИТЕЛЬ-ДЕТЕРГЕНТ ОТ ВРЕМЕНИ

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В работе исследовалась зависимость оптических свойств систем краситель-детергент от длительности хранения в темноте. Экспериментальные результаты показывают, что исследованные системы при постоянных температурах после длительного времени хранения в темноте, главным образом при концентрациях ниже критической концентрации мицеллообразования (ККМ), и при повышенных температурах выцветают, значения максимумов поглощения и интенсивности флуоресценции уменьшаются.