The Spectrophotometric and Tensiometric Study of Interaction Between Nonionic Surfactants with Acid Dye

ELENA IRINA MOATER, CRISTIANA RADULESCU*, IONICA IONITA
Valahia University of Targoviste, Faculty of Science and Arts, Sciences and Advanced Technologies Department, 18-20 Unirii Blvd., 130082, Targoviste, Romania

The study of the interaction between nonionic surfactants and acid dyes is very important in clarifying the mechanism of wool dyeing and colors preservation and also for the washing conditions determination. This paper presents the spectrophotometric and tensiometric data of the interaction between the alkyl polyglucosides surfactants class with new synthesized dye, from the class of azoic dyes derived from 3H-aza-1-oxa-2H-tioxo-5,8-fenalendisulfonic acid. A multiplicity of transitions is observed, when the surface tension of aqueous solutions of nonionic surfactant (APG) in the presence of the acid dye, which interacts strongly with nonionic surfactant to from a dye-surfactant complex, is measured at a constant concentration of the dye and plotted as a function of surfactant concentration. The formation of some surfactant- dye complexes was made evident in the different molecular ratios in the submicellar zone compared to the micellar zone of concentration of the surfactant. There au different equilibrium in the system which compete one another over a large scale of surfactant concentration (adsorption, micellization, small complex formation, large complex –mixed micelles formation).

Keywords: nonionic surfactant alkyl polyglucosides, acid dye, surface tension, UV-Vis spectrometry

In dyeing processes of textile fibers, the behavior of nonionic surfactants, which lead to a good fastness of dye on fibers and implicitly a well level of dyeing, are very important. Thus, the study of interaction between nonionic surfactants and dyes is significant for the dyeing mechanism elucidation of natural fibers. It is well known that this mechanism is affected by the addition of nonionic surfactant, due the formation of surfactant-dye complex. Generally, the surfactants are used in dyeing processes as auxiliary substance. In this respect, the main roles of the surfactant can be classified into four types of actions: as surface active compound; as fiber affinity compound; as dye affinity compound; as both fiber and dye affinity compound [1].

The aim of this paper is to investigate the interaction between alkyl polyglucosides nonionic surfactants and an acid dye from azoic dyes class. The investigation was achieved by measuring the surface tension for a several concentrations of surfactant and by comparing the results with the obtained from spectrophotometric data, as well. The nonionic surfactants have been chosen due the properties less aggressive towards to natural fibers.

The studies [1, 2] of interaction nonionic surfactant – C.I 120 blue acid dye, have been showed the formation of small complexes at concentrations under critical micellar concentration (CMC) of surfactant [1] ie bromophenol blue with non-ionic surfactants lead to a high complexes because the dye was rendered soluble in the micelle of surfactant [2].

Experimental part

A nonionic surfactants, from the alkyl polyglucosides class, with alkyl chain seized between 8-16 atoms of carbon (i.e. $C_{8/14}$APG, with following specifications: molecular mass 390 u.a.m.; 51-53% active substance; *p*H=11.5-12.5; viscosity 10 mPas; and $C_{12/14}$APG, Caspo-Europe product, with following specifications: polymerization degree *x* =1-4; 50-53% active substance; *p*H= 11.5-12.5; viscosity 2000-4000 mPas) were used. Nonionic surfactants were obtained from vegetal source, with ^{2}soft^{2} action on wool and cotton fibers.

The azoic dye (abbreviated C_{II}) derivate of the 3H-aza-1-oxa-2H-tioxo-5,8-fenalen disulphonic acid [3], with the reactive system represented by the isothiocyante group, was used. The chemical structure of azoic dye is presented in figure 1.

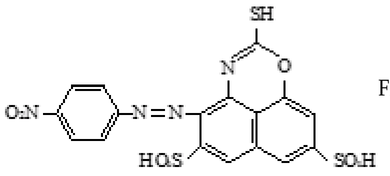

Fig. 1. Acid dyestuff - Cu

The acid dye C_{II} was purified by recrystallization from the ethylic alcohol was characterized by IR, UV-Vis, RMN spectra, elemental analysis, and melting points according with [2]. The purity of this compound was verified by ultra-high thin layer chromatography (UHTLC).

The formation of complexes was established by surface tension method and UV-Vis spectrophotometry, as well. The surface tension was determined by Du Nouy method, using a torsion balance (Speralfederwaage-Germeany) with a Pt-Ir ring attached, with 0.1 nN/m precision and 0.05 nN/m reproductibility. The UV-Vis measurements were performed by using an Evolution 260Bio UV-Vis-NIR spectrometer (Thermo Scientific).

Results and discussions

In this research, measurements of surface tension of $C_{8/14}$APG and $C_{12/14}$APG alkyl polyglucosides aqueous solutions different concentrations between (i.e. $1{\cdot}10^{-5}$ - $12.5{\cdot}10^{-4}$ mol/L at 25^{0}C) were achieved. The obtained data were showed that the surface tension decreases linear with the increase of surfactant concentration and finally reach a constant value at critical micellar concentration (CMC), which is typical for the amphiphilic molecules with a hydrocarbonat part with at least 8 methylene groups (table 1).

---

* *email: cristiana.radulescu@valahia.ro*

Table 1
THE CMC VALUES FROM TENSIOMETRIC DATA

Surfactant	CMC [mole/L]	Temperature [^{0}C]
$C_{8/14}$APG	$2.5\cdot10^{-4}$	25
$C_{12/14}$APG	$0.5\cdot10^{-4}$	25

The determinations of surface tension, for the aqueous solutions of C_{II} dye with concentrations between 10^{-4} mol/L and 10^{-3} mol/L, were showed that the values of them are identical with the same value of distillate water. Thus, in this case, the azoic dye not proved tensioactive properties.

For the nonionic surfactant – acid dye mixture was observed an increase of the surface tension, due the presence of dye, which indicated the existence of the association process between dye and surfactant. This associated form not proved tensioactive properties, as well. The surface tension isotherms of nonionic surfactant – C_{II} dye mixture at different concentrations of dye are presented in figure 2.

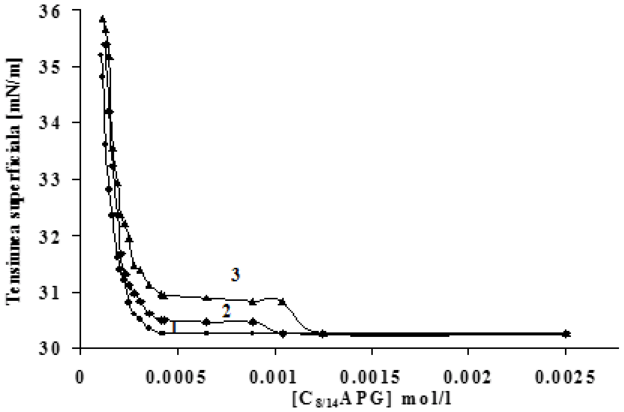

Fig. 2. The variation of surface tension for the $C_{8/14}$APG-C_{II} aqueous solutions in function of [$C_{8/14}$APG] concentration, at constant concentration of dye [C_{II}] at 25^{0}C:
1 - $C_{8/14}$APG in water; **2 -** mixed system $C_{8/14}$APG – C_{II} $1.0\cdot10^{-4}$ mol/L; **3 –** mixed system $C_{8/14}$APG – C_{II} $1.6\cdot 10^{-4}$ mol/L.

In figure 2 it can be seen that when the concentration of surfactant from mixture increases, the surface tension, initially, decreases, reach a level (first transition), then decreases again and finally, reach a constant value by the second transition, where the surface tension was identical with that value which correspond of critical micellar concentration of free surfactant.

It was observed that for to reach some value of surface tension in under-micellar area, for a solution which contained dye, it was necessary by a higher quantity of surfactant than in absence of dye. This idea presents the fact that exist a strong interaction surfactant-dye.

The multiple transitions demonstrated by both two methods used in this research or/and by other methods (conductometry, light diffusion, determination of viscosity), were notified as well as in the case of other surfactant-dye and surfactant-polymer solutions [4].

The surface tension at critical micellar concentration (CMC) of surfactant was identical with the surface tension at critical micellar concentration of surfactant – dye mixture ($CMC_{mixture}$). This aspect lead to the hypothesis that the surface tension of surfactant – dye mixture was a measure of the free surfactant quantity from solution through the adsorption equilibrium of molecules of free surfactant on the surface of solution, because the complexes were not absorbed at interface.

This hypothesis was sustained by the properties of complex, by the fact that it should be hydrophilic, and their formation being a consequence of hydrophobic bond which leads to solubilization in micelles. Other probable alternative can be that the interaction between the studied dye and nonionic surfactant can be achieved by etheric oxygens, in according with literature data [5] for anionic surfactants and nonionic polyethoxylated surfactants.

The formation of DS_n complex, according with the equilibrium:

$$D + nS \quad \leftrightarrow \quad DS_n \qquad (1)$$

can be described by the equation (2):

$$[C] = K([D]-[C])([S]-n[C])^n \qquad (2)$$

where: K – equilibrium constant; [C] – concentration of complex; [D] – total concentration of dye; [S] – total concentration of surfactant; n – number of molecules of surfactant witch are bounded to the dye; with the observation that it is assumed that the value of the activity of the coefficients is equal to unit.

If noted with [S]* the quantity of free surfactant witch was absorbed at interface and with [X] the quantity of surfactant witch interacted with dye and considering that [C] = [X]/n, [X] = [S] – $[S]^*$, can be resulted relation (3):

$$[S]-n[C]=[S]^* \qquad (3)$$

Thus, the equation (2) becomes equation (4):

$$[X]/n = K([D]-[X]/n)([S]^*)^n \qquad (4)$$

The difference of surfactant concentration from equation (4), represent the quantity of nonionic surfactant witch interacted with dye, and [S]* is attributed to the quantity of free surfactant, adsorbed at interface in the solution which contain dye. In equation (4), [D] and [S]* are known and [X] is measured, thus K can be calculated only if *n* is determined.

From tensiometric data *n* can be determined from equation (5):

$$\log([X]_i/[X]_j) = n\log([S]_i^*/[S]_j^*) \qquad (5)$$

due $[D]\rangle\rangle X/n(=[C])$ for any couple of solutions *i* and *j* witch contains a commune quantity of dye [D] representing, [X] and $[S]^*$ at a surface tension of surfactant γ_i and γ_j.

By using equation (2), which [D] and $[S]^*$ known and [X] measured, can be calculated the equilibrium constant, K, for each system. For K was obtained values between $2\cdot10^8$ – $1.66\cdot10^{13}$ (table 2) with not depended by the modification of concentration by [D] and $[S]^*$.

The formation of DS_l complexes different by DS_n, can be achieved above of the first transition point, and the formation of DS_l could lead to the increase of [X]. The $^2l^2$ number is determined by the difference $[S]_{ccm}$ – $[S]^*_{ccm}$ if supposedly [DS_n] « [DS_l] at $[S]_{ccm}$. Representing $[S]_{ccm}$ – $[S]^*_{ccm}$ = f(D) it was obtained a straight line and from slope was calculated the *l* value. Thus, the values included in 10-50 intervals were obtained. The hypothesis that [DS_n]«[DS_l] was accepted, because the equilibrium constant of DS_l is higher than the one of DS_n, according with equation (2).

Table 2
THE NUMBER OF SURFACTANT MOLECULES BOUNDED BY DYE (n, l) AND EQUILIBRIUM CONSTANT (K) VALUES OBTAINED FROM TENSIOMETRIC DATA AT 21^{0}C

Composition	CMC [mole/L]	n^*	K	l^{**}
$C_{8/14}$APG – aqueous solutions	$2.50\cdot10^{-4}$	-	-	-
$C_{8/14}$APG -C_{II} 1x10^{-4} mole/L	$12.50\cdot10^{-4}$	1.20	$3.57\cdot10^{8}$	10-40
$C_{8/14}$APG -C_{II} 1.6 x10^{-4} mole/L	$22.50\cdot10^{-4}$	2.00	$2.42\cdot10^{8}$	10-40
$C_{12/14}$APG –C_{II} 1x 10^{-4} mole/L	$7.50\cdot10^{-4}$	1.00	$1.55\cdot10^{8}$	10-50

**n- the number of molecules of surfactant bounded by dye in under-micellar domain;*
l – the number of molecules of surfactant bounded by dye in micellar domain.

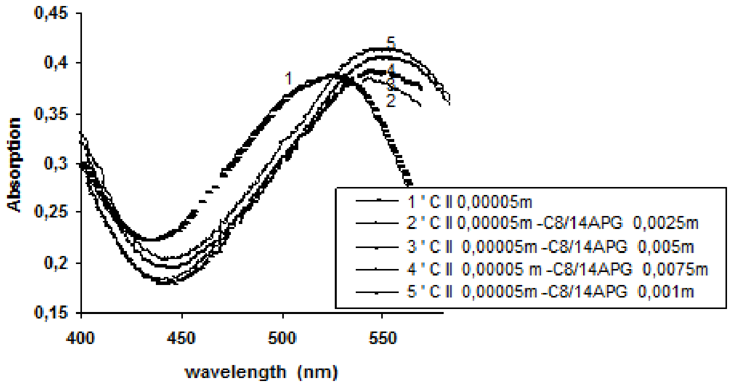

Fig. 3. Absorption spectra for the aqueous solution of $C_{8/14}$APG; C_{II} and mixed systems $C_{8/14}$APG -C_{II} ($5\cdot10^{-5}$ mol/L) on UV-Vis at 21^{0}C

The spectrophotometric study of $C_{8/14}$APG -C_{II} system showed some displaces of maximum wavelengths for dye in the presence of nonionic surfactant (fig. 3).

The maximum displacement from UV domain to smaller values of wavelengths, in the case of surfactant-dye mixture, proved the formation of some complexes in which dye passed at superior excited state.

In visible domain, for the $C_{8/14}$APG-C_{II} systems, some maximum displacement of wavelength of dye, from 535 nm at 544 nm was observed. This think explained the formation of some complexes and a diminution of the interval between the fundamental and exited states, the necessaries of energy being much lower. The absorption intensification, therefore and color, the hyperchrome effect for the surfactant-dye mixture in visible domain (where the surfactant not absorbed) shown a structural modification in the dye molecules which increases the possibility of a transition (table 3).

Table 3
THE VALUES OF ABSORBANCES AT λ_{max} FOR $C_{8/14}$APG AND SYSTEMS $C_{8/14}$APG -$C_{II.}$

Studied system	UV domain			VIS domain		
	λ_{max}	Abs.	Effect	λ_{max}	Abs.	Effect
[$C_{8/14}$APG] $25\cdot10^{-3}$m	220	0.366	-	-	-	
[$C_{8/14}$APG] $5\cdot10^{-3}$m	220	0.715	-	-	-	
[$C_{8/14}$APG] $7.5\cdot10^{-3}$m	220	1.086	-	-	-	
[C_{II}] $5\cdot10^{-5}$ m	233	1.051	-	535	0.387	
[C_{II}]$5\cdot10^{-5}$m-[$C_{8/14}$APG]$2.5\cdot10^{-3}$m	221	1.366	hypsochrome	544	0.385	bathochrome
[C_{II}] $5\cdot10^{-5}$m -[$C_{8/14}$APG] $5\cdot10^{-3}$m	221	1.628	hypsochrome	544	0.392	bathochrome and hyperchrome
[C_{II}]$5\cdot10^{-5}$m-[$C_{8/14}$APG]$7.5\cdot10^{-3}$	221	2.029	hypsochrome	544	0.413	bathochrome and hyperchrome
[C_{II}]$5\cdot10^{-5}$m -[$C_{8/14}$APG]$10\cdot10^{-3}$	221	2.364	hypsochrome	544	0.404	bathochrome and hyperchrome

Conclusions

The mechanism for the interaction of the systems formed from alkyl polyglucosides nonionic surfactants and acid dye C_{II} derivatives of 3H-aza-1-oxa-2H-tioxo-5,8-phenoldisulphonic acid, can be divided in four processes: superficial adsorption of molecules of free surfactant; formation of small complexes DS_n (n= 2-3); the formation of high complexes (mixed micelles) DS_1; the formation of regular surfactant micelles.

All this process varies with the surfactant concentration in competition one with another.

The maximum displacement of wavelengths in the micellar mixture C_{II} – $C_{8/14}$APG showed an interaction between dye with nonionic surfactant and the formation of some complexes which can be capable to accept the protons. The formation of complexes promotes the dissociation and transformation of dye in a basic form. Thus of data were obtained by using both tensiometric and UV-VIS spectrophotometric techniques. It can be concluded that the tensiometric method has some advantages for research of such interactions towards the spectrophotometric technique. By spectrophotometry it is impossible to measure the absorption of one mixed solution with a higher concentration of dye, because the dilution of the mixture solutions can be leaded to the modification of the aggregation number or of the mixed aggregate which are formed in solution.

References

1.NEMOTO, Y., FUNAHASHI, H., Journal of Colloid and interface Science, vol 62, no.1, 1977, p. 95.

2.LUCK, W., J. Soc. Dyes. Colour 74, 1960, p.221.

3.DUMITRESCU, C., TÃRÃBAªANU-MIHAILÃ. C., MARIS, F., Ovidius University Annals of Chemistry, XI (1), 2000, p.63-65.

4.JONES, M.N., J. Colloid Interface Sci., 23, 1967, p.36.

5.MENGER, F.M., KEEPER, J.S., AZOV, V., Langmuir 16, 2000, p.2062.

Manuscript received: 31.05.2016