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INFLUENCE OF SURFACTANTS ON THE ALKALINE FADING OF FUCHSIN

Diana Minea, Adina Raducan, Petruta Oancea

Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest,
bd. Elisabeta 4-12, Bucharest, araducan@yahoo.com, Romania

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Introduction

Triphenylmethane dyes are used extensively in textile industries for dyeing cotton, nylon, wool, silk, and are also used in leather industries. As a consequence, they are found as pollutants in residual waters from these industries. Even small amounts of dyes in water are enough to produce color which is totally undesirable for any kind of natural or surface water. There is a considerable demand for color-free effluent, but the color removal from wastewater may involve extremely difficult and costly treatments. Fuchsine is a triphenylmethane dye used in hair dye, as a colorant in artist paints, as cosmetics products not intended to come in contact with mucous membranes, to stain animal and vegetable fibers. It is also stable to light and oxidizing agents, so it is resistant to aerobic digestion. The usual technologies for color removal include adsorption, photocatalysis and chemical/enzymatic oxidation. Since these wastewaters also contain substances that modify the medium, a study of dyes fading in the presence of surfactants, which are already present in such waters, can contribute to the development of new decontaminating procedures.

Materials and methods

Basic fuchsine (dye content $\geq 88\%$), sodium hydroxide (99.5%), sodium dodecyl sulphate (98%), hexadecyl-pyridinium chloride monohydrate (99%), Hexadecyltrimethylammoniumbromide (99%) and Triton X100 laboratory grade were purchased from Sigma-Aldrich. Stock solutions of 1mM fuchsine, 0.02M SDS, 2mM HDPC, 1mM CTAB and 1mM Triton X100 were prepared in bi-distilled water. The ultraviolet-visible (UV-VIS) measurements of fuchsine solutions in the presence of surfactants and during the alkaline fading were performed with a JASCO V-530 spectrophotometer equipped with a Peltier cell for temperature and stirring control. The reaction progress was monitored through the absorbance changes of the dye/surfactant/NaOH mixtures at 545 nm. The concentration of surfactants were chosen to cover both pre-micellar and micellar regions, considering the following values for critical micellar concentrations (cmc): $cmc_{(SDS)} = 8.08$ mM, $cmc_{(HDPC)} = 0.87$ mM, $cmc_{(CTAB)} = 1.05$ mM and $cmc_{(Triton\ X100)} = 0.24$ mM.

In order to ensure pseudo-first kinetics and to maintain a constant pH at a constant value, in all degradation experiments the concentration of NaOH exceeds at least 50-fold the dye concentration.

The ionic strength of the medium was kept constant by adding potassium nitrate.

Results and conclusions

Since the hydroxide is in excess in all data sets, the reaction is of pseudo first order and the integral kinetic equation is:

$$A_t = A_0 \cdot \exp(-k t) \tag{1}$$

where A_t and A_0 are the absorbance's at the time t , and 0 respectively, k is the pseudo first order rate constant and t is the time (seconds). The kinetic constants k were estimated fitting equation (1) on the experimental data $A = f(t)$ and the kinetic constants for the second order reaction were calculated as $k_2 = k/[HO^-]$, where $[HO^-] = 3mM$. In Figure 1 are the kinetic curves obtained for different concentrations of SDS and Triton X100

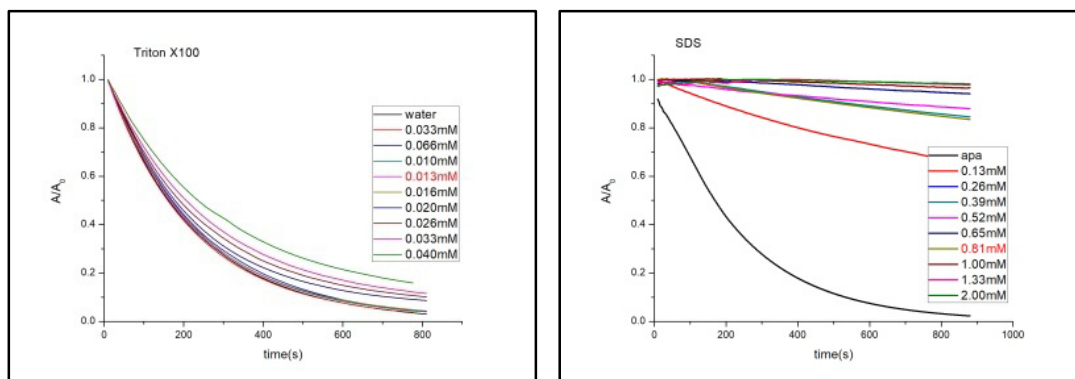


Figure 1. Kinetic curves for alkaline fading of fuchsin in the presence of surfactants

The catalytic effect of surfactants at submicellar concentrations is a well known phenomenon and experimental results are in accord with many available literature data. Small aggregates of the surfactant (dimers, trimers, and tetramers) exist below the cmc; these small submicellar aggregates can interact physically with the reactants, forming kinetic micelles which are catalytically active entities. Taking into account that the reaction occurs both in solution and in kinetic micelle, we used the pseudo-phase model, which suppose that the distribution of surfactant between different states of aggregation is controlled by a series of cooperative dynamic association-dissociation equilibria, which can be considered as a global step for the formation of micelles. According to this model the observed kinetic constant (k_{exp}) is given by:

$$k_{exp} = \frac{k_m [D]^n + k_w K_D}{K_D + [D]^n} \tag{2}$$

where $[D]$ is the concentration of surfactant, K_D is the dissociation constant of the micelle, n is the number of surfactant molecules that form a kinetic micelle, k_m is the rate constant inside the micelle and k_w is the rate constant in water. The results show that cationic surfactants have a slightly catalytic effect on the fading of fuchsin, while the presence of anionic surfactant leads to pronounced inhibitory effect.