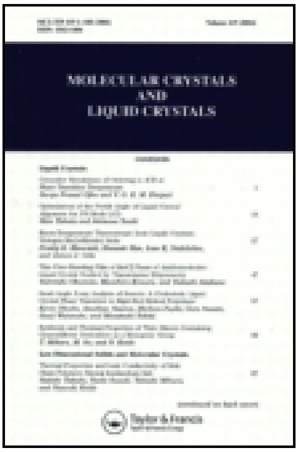

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Analysis of the Solubilisation Power of Detergents by Photochromic Probe

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The ability of micelles to solubilize organic substances is a property of fundamental importance in many practical applications, such as in detergents. In this work, a new method to determine the solubilisation power of SDS, in terms of the amount of captured organic substance, was used for the first time.

A photochromic probe has been dispersed into an organic phase and its incorporation in the micellar system was monitored. The volume of the organic phase entrapped within the micellar hydrophobic core has been measured by the absorbance peak of the dye sensitizer.

In our work, three organic compounds were used to determine the amount of organic solvent solubilised by SDS/water system.

Keywords: photochromic probe; solubilization power; detergents; SDS.

Introduction

Surfactants play an important role in chemistry with considerable implications for the environment [1]. Above a certain concentration, that is the critical micelle concentration (cmc), surfactants undergo a reversible self-aggregation to form micelles [2]. With increasing surfactant concentration, the micelles exhibit a special set of macro-structural transitions, changing from a spherical shape into cylindrical and other shapes. Depending on the chemical nature of surfactant, temperature and water content, different types of ordered liquid-crystalline phases can also exist (cubic, lamellar and hexagonal phases) [3]. Such a fascinating variety of self-assembled structures lead to occurrence of a wide range of physical chemistry behaviour [4].

Soaps (sodium oleate etc.) are fatty acid salts [5] (later on, we will recognise them to be a type of anionic surfactant). They are characterised by a long hydrocarbon chain which represents the hydrophobic portion of the molecule, also called “tail”. This hydrocarbon chain may be mono-unsaturated (it contains one C-C double bond), poly-unsaturated (more than one double bond) or saturated (no double bonds). A carboxylate group, attached at the end of the hydrocarbon chain, represents the hydrophilic portion of the molecule, also called “polar head”. A surfactant that does not possess the above described molecular chemical characteristic, is considered a detergent. Detergents could be produced easily from

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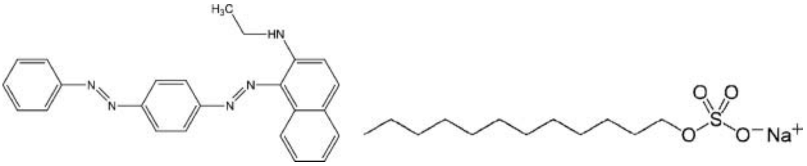

Figure 1. Oliviero R. Cesare et al. “Molecular structure of Sudan Red 7B (on the left) and schematic draw of the structure of SDS (on the right)”.

petrochemicals. The procedure was developed during World War I and World War II as an answer to the scarcity of the animal and vegetable fats. Aqueous solutions of detergents or soaps are used for cleaning dirt, which is essentially made by organic non polar substances. Because of its polar nature, pure water can’t remove those grimy compounds. Soap allows oil and water to mix acting as an emulsifier so that oily stains can be removed during rinsing.

The ability of a micelle to solubilize water-insoluble organic molecules is usually described through the solubilization power of the detergent, *Ps*, defined as the molar amount of solute dissolved in the micellar pseudophase per mole of micellized detergent at

Table 1. Oliviero R. Cesare et al. “Spectrometric properties of the dye solutions”

Dye solution conc., (mol/L $*10^{-7}$)	Absorbance at 534 nm, (-)	Molar absorption coefficient, ε (L/mol*cm)
	Toluene	
2.2	0.0224	$4.56*10^{-4}$
7.3	0.0371	
8	0.0746	
22.8	0.1024	
34	0.1366	
56	0.2536	
	P-xylene	
9,46	0,04	$4.11*10^{-4}$
12	0,058	
24	0,095	
56	0,23	
83	0,33	
98,6	0,4	
	Benzene	
5,9	0,0399	$3.40*10^{-4}$
18	0,0733	
34	0,1241	
45	0,1654	
96,3	0,3229	
144	0,484	

Table 2. Oliviero R. Cesare et al. "Spectrometric properties of the SDS/water/dye solutions at saturation. The solubilization power of SDS/water solutions is expressed as the volume of organic solvent inside micelles"

SDS/water solution conc.,(%)	Absorbance at 534 nm, (-)	Dye conc. in the organic solvent dispersed inside micelles, (mol/L*10^{-7})	Volume of organic solvent inside micelles, (ml*10^{-4})
		Toluene	
0.1 (below CMC)	0	0	0
0.3 (c.a. CMC)	0.0066	2.00	2.11
0.75 (above CMC)	0.0076	2.20	2.32
1.5	0.0144	4.10	4.32
8	0.1548	34.5	36.3
16	0.5644	111	117
		P-xylene	
0.1	0	0	0
0.3	0.0035	0.83	0.874
0.75	0.0058	1.30	1.37
1.5	0.0105	1.76	1.85
8	0.0242	5.70	6.00
16	0.0704	16.6	17.5
		Benzene	
0.1	0	0	0
0.3	0	0	0
0.75	0.0074	1.10	1.16
1.5	0.0105	2.00	2.11
8	0.0334	9.70	10.2
16	0.0568	21.0	22.1

saturation [6,7]. In the present work we tested a new method for the direct measurement of the volume of three different organic compounds dissolved into micelles made by Sodium Dodecyl Sulphate (SDS, figure 1) dispersed in water [8]. A oil-soluble dye sensitizer, Sudan Red 7B which is a well known marker to visualize lipid bodies in plant cells [9], has been dissolved into the organic phases. When the SDS/water micellar system incorporates the dye-organic solvent composite, one can get informations of the amount on solute entrapped into micelles by the absorbance peak of the dye in the UV-Vis spectrum.

Materials and Methods

As reported in Table 1, Sudan Red 7B was dissolved in each of the three organic compounds Benzene, Toluene and p- Xylene at different concentration ratios. The measured absorbance at the different concentrations allowed us to calculate the linear calibration line and to determine the molar absorption coefficient ε by the Lambert-Beer law :

$$A = C \varepsilon d \tag{2}$$

Where A is the absorbance at 534nm, C is the concentration of the dye and d is the optical path corresponding to the length (1cm) of the quartz cuvette probe For our measurements a Varian Cary 50 Scan spectrophotometer, virtual double beam equipped, has been used. All the measurements were performed in a thermostated room at 25.0°C. Little amounts of the dye stock-solution at the fixed concentration of 9.5×10^{-4} mol/L, were added to SDS/water micellar solutions under stirring (Table 2) and left to reach the phase separation for at least 3 days. Spectrophotometer measurements were then performed on SDS/water micellar solutions in the saturation state. By measuring the intensity of the absorbance peak of the dye micellar solutions, it was possible to calculate the concentration of the dye inside micelles. These data were used to calculate the volume of the organic solvent inside micelles (Table 2).

Results and Discussion

It is well known [10] that at concentrations well above the cmc of SDS/water solutions (Figure 2) the system is able to solubilize great amounts of organic solvents. The solubilisation power strongly depends not only on the surfactant type but also on the type of organic solvent.

In this study UV/Visible spectroscopy technique was used for the first time to calculate the volume of three different benzene-derivates organic solvents inside SDS/water micelles.

The presence of a dye dispersed in the organic solvent, allowed to perform this characterization and to obtain the quantity of solvent inside micelles by the simple Lambert-Beer law. Results are collected and shown in Tables 1, 2 and Figure 3 for all of the investigated systems.

Although further investigations are needed for the standardization of the procedure, it clearly appears that toluene is the organic solvent that better is absorbed into SDS/water

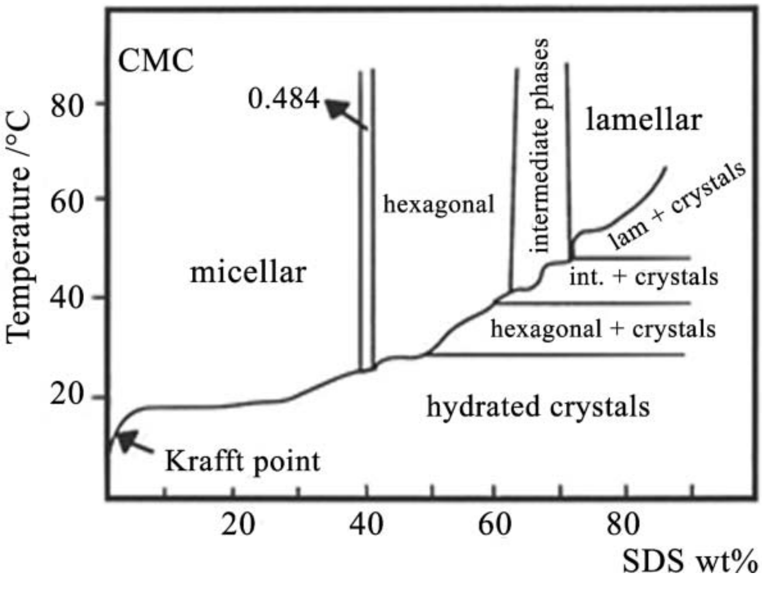

Figure 2. Oliviero R. Cesare et al. “Phase diagram of the SDS/water system, (R.G. Laughlin, The aqueous phase behavior of surfactants, Academic Press, London, 1994)”.

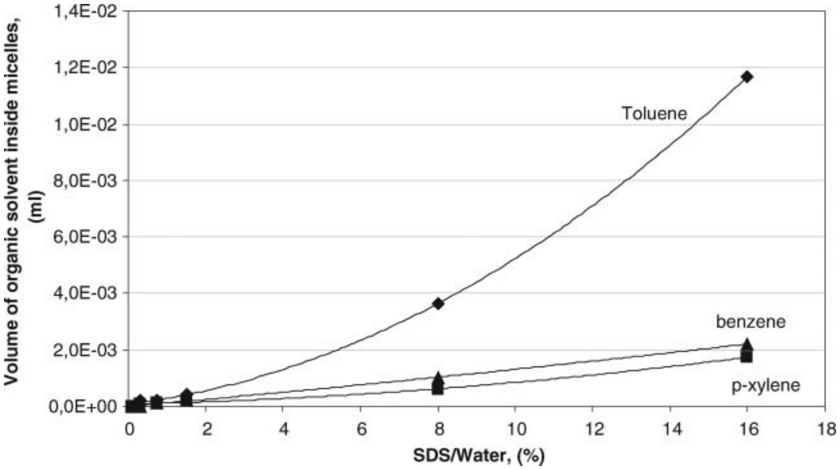

Figure 3. Oliviero R. Cesare et al. "The volume of the organic solvents inside SDS/water micelles at the saturation".

micelles. On the other hand benzene and p-xylene have a similar affinity for the micellar system that was tested. This behaviour might be interpreted by considering the methyl group and its position on the benzene ring as the only chemical difference in the three organic solvents. How this little chemical difference can lead to a different absorption by the SDS/water micelles? A possible explanation involves the dipole moment of the organic solvents. Indeed, benzene has no dipole moment and p-xylene possesses a very low dipole moment, 0.07 D, whereas toluene dipole moment is 0.36 D. From these data we can say that toluene molecule is relatively more polar than the other two benzene derivatives. A micelle created as we did for the present study is a complex macro-structure, but we can essentially think about it as a two shells onion. The external shell, in contact with water, is the polar layer while the inner shell is the non polar layer where the organic solvents are confined. The greater is the hydrophobic character of a compound, the better it will be confined in the core of the micelle. Hence toluene molecule distribute better than benzene and p-xylene throughout the hydrophobic layer because it can go closer to the polar head shell leading to a greater volume of substance that can be absorbed by the SDS/water micelles.

Conclusions

In the present study we tested a new method for the measurement of the solubilisation power of detergents. For the first time, a photochromic probe allowed us to easily calculate the volume of organic solvents confined inside a micellar phase made up by the well-known SDS/water binary system. In a more general frame, results revealed also that the affinity of the benzene-derivative organic solvents with surfactant/water system strongly depends on the groups bounded to the aromatic ring. Even small chemical differences can produce great discrepancy in the volume of organic solvent absorbed by the micellar system. A more general conclusion is that benzene-derivates organic solvents with relatively high dipole moment, better solubilize in the micellar phase of a SDS/water system. Further investigations are in progress also by testing other surfactants as micellar system. This will clarify the role of the chemical nature of surfactant in solubilising organic solvents.

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