

Research Article

The Solvent Influence on Thymidine-SDS- Alcohol Micelle System: Studies With UV-Vis Technique

Bhattarai A¹, Wachnik HW^{2*} and Grzegorek M²

¹Department of Chemistry, M.M.A.M.C, Tribhuvan University, Biratnagar, Nepal

²Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

*Corresponding author e-mail: wilczura@chem.uw.edu.pl

ABSTRACT

The measurements of thymidine absorbance in presence of SDS/solvent/water systems at 25°C by UV-Vis technique are reported. The solvents selected were the following aliphatic alcohols: ethanol, n-butanol, n-heptanol and n-decanol. In this paper first time are presented data for SDS micelles in alcohols with some addition of water. In all studied systems concentrations of SDS (sodium dodecyl sulphate) were above CMC. Water concentration in the studied systems was defined by R parameter according to relation: $R=[H_2O]/[AOT]$ and was between 0 to 50 depending on the system. In the present work SDS micelles mimicked in a very simple way the structural aspects of some domain in bio membranes. The distribution of thymidine, which is one of the pyrimidine bases of living matter (is found in the nucleic acid DNA) between organic and micellar phase was the object of our study. Using UV-Vis technique the investigation of thymidine/alcohol/SDS/water system at 25°C were done, and next the results were discussed in the context of influence an aliphatic alcohol on thymidine interaction with SDS micelles. Moreover, obtained results involve us to predict the privilege location of thymidine molecules in SDS micelles. The experimental values of thymidine absorbance as a function of surfactant

concentration was analyzed with NLREG procedure. There were two adjusted parameters: the binding constant and distribution constant of thymidine partitioned between alcohol and SDS micellar phase, and finally on thymidine distribution between solvent and SDS micelles. Obtained results are discussed in the context of solvent influence on thymidine-SDS-alcohol-water system. The UV data showed the strong influence of the hydrocarbon chain length in alcohol and water concentration on the absorbance of thymidine in studied systems. The solvent influence on thymidine absorption results from the type of SDS micelles in the system. In ethanol and butanol SDS normal micelles are favoured; in heptanol and decanol SDS reversed micelles are more probable. There was found that thymidine molecules interact stronger with SDS micelles in decanol in comparison to shorter alcohols. Such tendency is probably connected with different type of micelles (normal or reversed) existing in studied solvents: short and long aliphatic alcohols.

Keywords: Thymidine, Aliphatic alcohols, Sodium dodecyl sulphate, UV-Vis

INTRODUCTION

Thymidine is a pyrimidine nucleoside composed of the pyrimidine base thymine attached to the sugar deoxyribose (Figure 1). As a constituent of DNA, thymidine pairs with adenine in the DNA double helix. There are results of work on some thymidine analogs^{1,2}, and there is a lot of research on thymidine kinase^{3,4}, and thymidine phosphorylase⁵. Thymidine in water solutions have been investigated by Resonance Raman spectroscopy and density functional theory (DFT)⁶. There is a lack of information about UV-Vis studies on thymidine/alcohol/water systems. Sodium dodecyl sulphate (SDS) is an example of a widely studied anionic surfactant. Its

structure consists of a hydrophilic (polar) ionic group and hydrophobic (non-polar) hydrocarbon chain (Figure 2). Above a certain concentration (critical micelle concentration or cmc), SDS molecules tend to self-assemble and form clusters called micelles and reversed micelles depending on solvent polarity. In non-polar solvents, reversed micelles of SDS can cover small molecules as for example water molecules in polar reversed micelles core^{7,8}. There are in the scientific literature a lot of studies on SDS micelles in water. Among many the structure of SDS micelles in water has been characterized by various methods, e.g. small-angle neutron scattering (SANS). It has been shown that micelles were slightly

compressed, and their sizes decreased with the temperature growth⁹. The phase diagram of the SDS/water system has been determined by differential scanning calorimetry (DSC)¹⁰. Shape and size of SDS micelles in water have been studied also by molecular dynamics (MD) simulations^{11,12}. SDS has been studied with Sum Frequency Generation (SFG) spectroscopy at the air/water interface¹³, and at the CCl₄/water interface¹⁴. Micro emulsions consisting of oil droplets in water stabilized with SDS have been studied by sum frequency scattering (SFS)¹⁵. Thermodynamics of lipid membrane solubilization by SDS has been investigated by right-angle light scattering (RALS) and isothermal titration calorimetry (ITC)¹⁶. There are many works in literature referring to SDS in water and addition of alcohols systems studies. An SDS characteristic in the mixture of ethanol and water has been studied by ion selective electrode (ISE) technique to determine sizes and aggregation numbers of the micelles in these solutions¹⁷. Coarse-grained (CG) dynamical simulations have been used to study the alcohol effect on SDS micelles structure. Hexanol, octanol, decanol, dodecanol, tetradecanol, and hexadecanol have been chosen for this study¹⁸. Volumetric measurements have been made

to determine the effect of methanol, ethanol, n-propanol and iso-propanol on SDS/water systems¹⁸⁻²⁰. Research on other SDS/alcohol/water systems has been reported by several authors²¹⁻³⁵. It should be noted that all of the studies cited above were SDS micelles in water with the possible addition of other solvents such as of alcohols. In this paper are presented data for SDS micelles in alcohols with some addition of water.

Using UV-Vis technique investigation of thymidine/alcohol/SDS/water system at 25°C were done and next results were discussed in the context of influence an aliphatic alcohols and water presence on thymidine interaction with SDS micelles in water presence.

EXPERIMENTAL PROCEDURE

Materials and media preparation

Sodium dodecyl sulphate (SDS 98%) was from Sigma-Aldrich, Germany, and was used as received, Thymidine (>99%) was from Sigma – Aldrich, Germany and used without further purification and solvents (ethanol, n-butanol, n-heptanol and n-decanol) were purchased from POCH, Poland for spectroscopy quality. All

alcohols were checked by UV-Vis before using. Water was of bidistilled quality.

All solutions were prepared gravimetrically at 25°C, and stirred 24 hours on magnetic stirrer. SDS solutions in aliphatic alcohols with different concentrations were all above the CMC (critical micelle concentration). For selected solvents CMC for SDS were determined using procedure described earlier³⁶. Numerical values are given in Table 1. Obtained data were not compared with literature because of lack of such data.

Analytical procedure

For all studied systems thymidine absorption spectra were recorded in the range 200-350 nm at 25°C with Varian UV-Vis Spectrophotometer (Model Cary 50 Conc.) single beam equipped with 1 cm length quartz quvette. UV measurements were performed with the following procedure. Before each measurement base line was registered for suitable SDS/solvent system (with or without water) and afterwards a thymidine solution in the same solvent was added. After adding thymidine solution to the SDS once the whole liquid volume was stirred very carefully. The absorption band was registered as a function of surfactant concentration. For the systems with the addition of water its amount of added to

SDS solution was calculated according to relation $R=[H_2O]/[SDS]$. Depending on the alcohol R parameter value was between 0 and 50.

RESULTS AND DISCUSSION

The final thymidine concentration in a quartz quvette was 7.07×10^{-5} M in all alcohols. This concentration involved obtaining a well-marked thymidine absorption bands in used solvents (Figure 3). The band I maximum was at around 215 nm and suitable for band II at 267 nm. The highest absorption for thymidine were registered in n-butanol the lowest in ethanol. For other alcohols obtained intermediate values.

In further study the intense of band II as a function of SDS concentration and R value was detected. In Figure 4 is shown the band II for thymidine/butanol/water system depending on water addition. For the other systems similar spectrums were registered for different SDS concentrations.

All obtained spectrums were analyzed in the context on thymidine absorption at 267 nm as a function on surfactant concentration. The results are presented in Figures 5-8 for ethanol, butanol, heptanol and decanol as

solvents suitable. The thymidine absorbance for band II registered after mixing SDS/alcohol/water solution changed not only with SDS concentration but also with water addition. The experimental values of thymidine absorbance as a function of surfactant concentration for different R value were analyzed with NLREG procedure. We assumed that after mixing thymidine molecules interact with SDS micelles and the total absorption is a sum of thymidine bonding to micelles and “free thymidine” dissolved in solvent. The total absorbance is a sum of two contributions: absorbance of thymidine dissolved in SDS micellar phase and absorbance of thymidine dissolved in organic phase. Following the procedure developed by Magid *et al.*³⁶ for analyzing UV-Vis spectra of phenols in AOT/isooctane/water system the binding constant (K') of thymidine to SDS micelles and thymidine absorbance in pure solvents were obtained as a fitting parameter from the following relation:

$$A = A_0 + \frac{(A_m - A_0)K'[SDS]}{1 + K'[SDS]} \quad (1)$$

where: A_0 and A_m are thymidine absorbance in pure alcohol and micellar phase respectively, K' -binding constant and $[SDS]$ surfactant concentration. A is a total absorbance registered experimentally as a

function of SDS concentration. For systems with water addition R value was taken into account in equation (1). So, there were two adjusted parameters: the binding constant and thymidine absorbance in micellar phase. A_0 was measured in a separate experiment. For the studied systems the thymidine distribution constant between micellar and organic phases were calculated from the relation:

$$K' = K \cdot M_{SDS} \quad (2)$$

In NLREG procedure thymidine binding constant (K'), and A_m were obtained and then constant distribution K was calculated. The numerical values of K' and K are presented in Table 2 and in Figures 9 and 10.

Obtained results indicate on both solvent and water influence on thymidine/ SDS-alcohol-water system. Except n-butanol the UV data showed the strong influence of the alcohol chain length, and water contents on the thymidine absorption in studied systems. In case of n-butanol the thymidine absorption was not changed with water contents, see data for $R=5$ and 50 (Figure 10). For the other systems both without ($R=0$) and with water ($R=10$, and $R=20$), the binding constant (K') and distribution

constant (K) values increased in the following order:

Ethanol<Heptanol<<Decanol.

Thymidine absorption on micellar phase (A_m) changed as follows:

Ethanol<<Heptanol>Decanol in the systems without water. Such tendency indicates on complex interactions between thymidine molecules and micelles. It is probably connected with different type of micelles (normal or reversed) existing suitable in short and long aliphatic alcohols. Moreover, in case of SDS micelles in ethanol an addition of water causes strong interactions between water molecules and surfactant's polar heads which result with hydrogen bonds formation. In such systems interaction of thymidine molecules with SDS micelles are weaker in comparison to SDS reversed micelles present in longer aliphatic alcohols. Interesting tendency was observed for thymidine absorption on micellar phase (A_m parameter) depending on the solvent. The highest values were obtained for n-heptanol and the lowest for ethanol. If we compare the distribution constants in studied systems, it seems that in the systems containing reversed micelles thymidine molecules

moves from the solvent to micellar phase and stronger interact. Still it needs additional investigations.

CONCLUSION

The results of UV-Vis measurements of thymidine/alcohol/SDS/water systems show the significant influence of solvent, and water addition on thymidine absorption.

The solvent influence on thymidine absorption results from the type of SDS micelles in the system. In ethanol and butanol SDS normal micelles are favoured; in heptanol and decanol SDS reversed micelles are more probable.

Thymidine molecules interacts stronger (see binding constant as function of carbon atom numbers) with SDS micelles in decanol in comparison to shorter alcohols. Such tendency is probably connected with different type of micelles (Normal or reversed) existing in studied solvents: short and long aliphatic alcohols.

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Binding of phenols to inverted micelles

and micro emulsion aggregates. *J Phys Chem* 1981; 85: 1434-1439.

Figures and Tables

Figure 1: Chemical structure of thymidine.

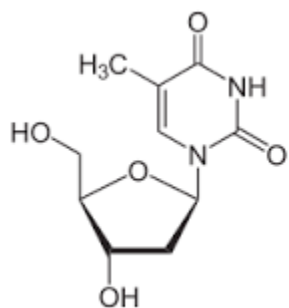


Figure 2: Chemical structure of SDS.

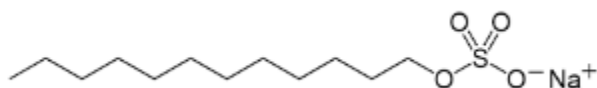


Figure 3: Thymidine spectrum in butanol (red), heptanol (green), decanol (dark blue) and in ethanol (dark pink).

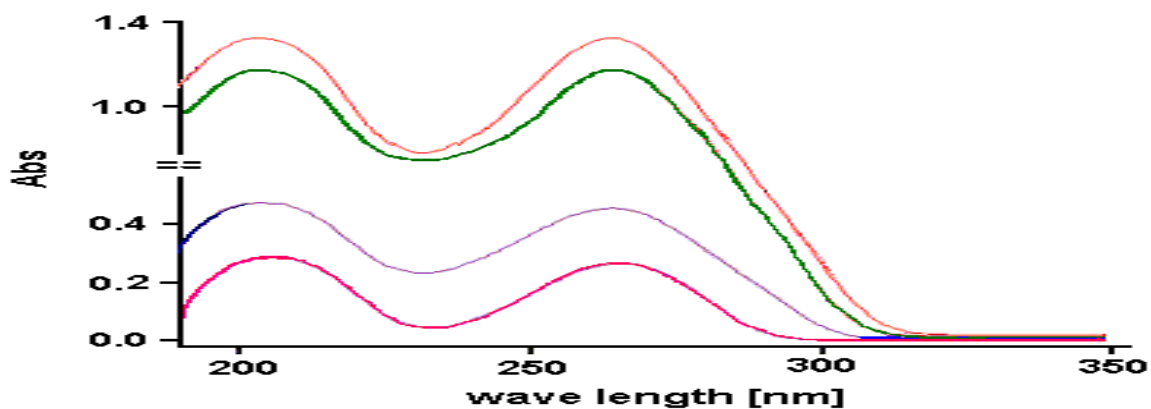


Figure 4: Thymidine band II in SDS/butanol for R=0 (green line), R=5(red line) and R=50 (dark pink line).

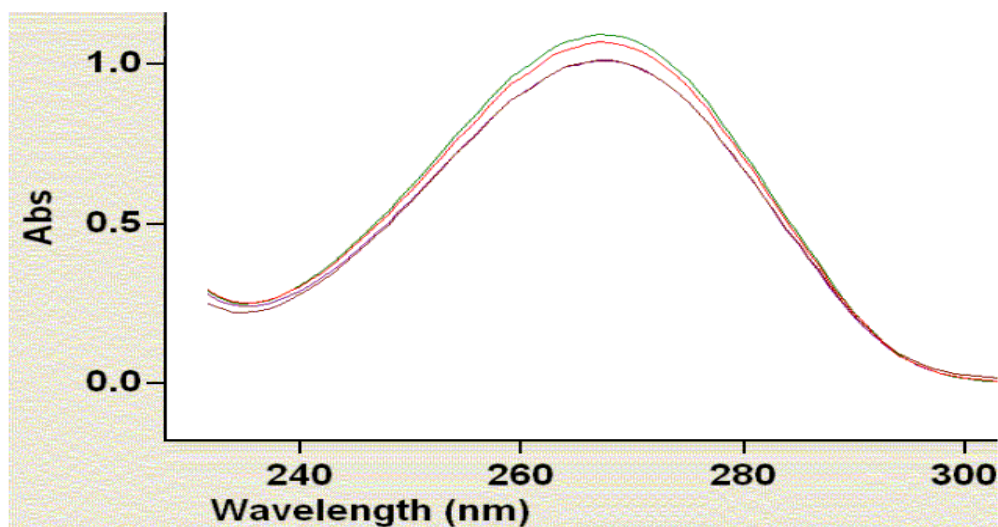


Figure 5: Absorption of thymidine band II at 267nm as function of SDS/ethanol concentration for different R.

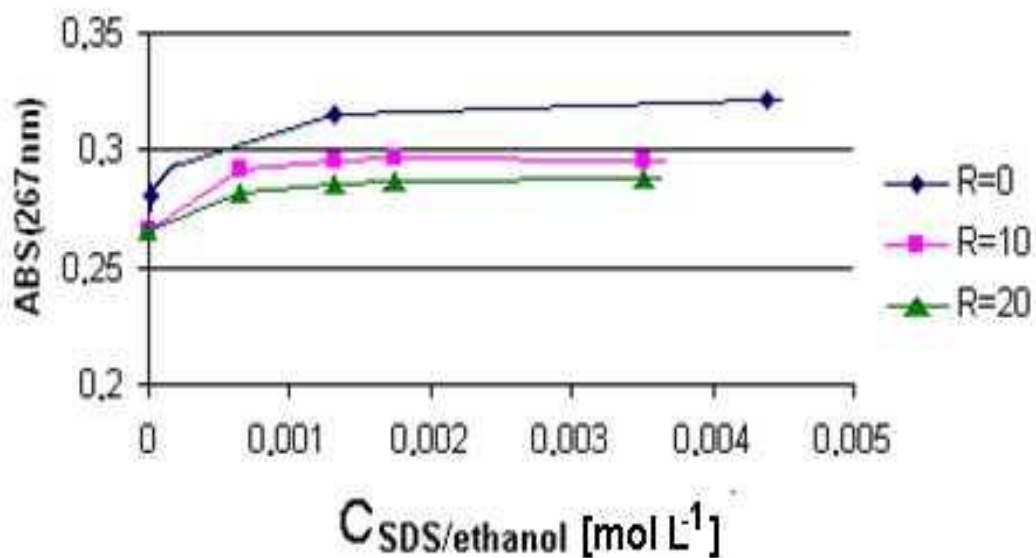


Figure 6: Absorption of thymidine band II at 267nm as function of SDS/butanol concentration for different R.

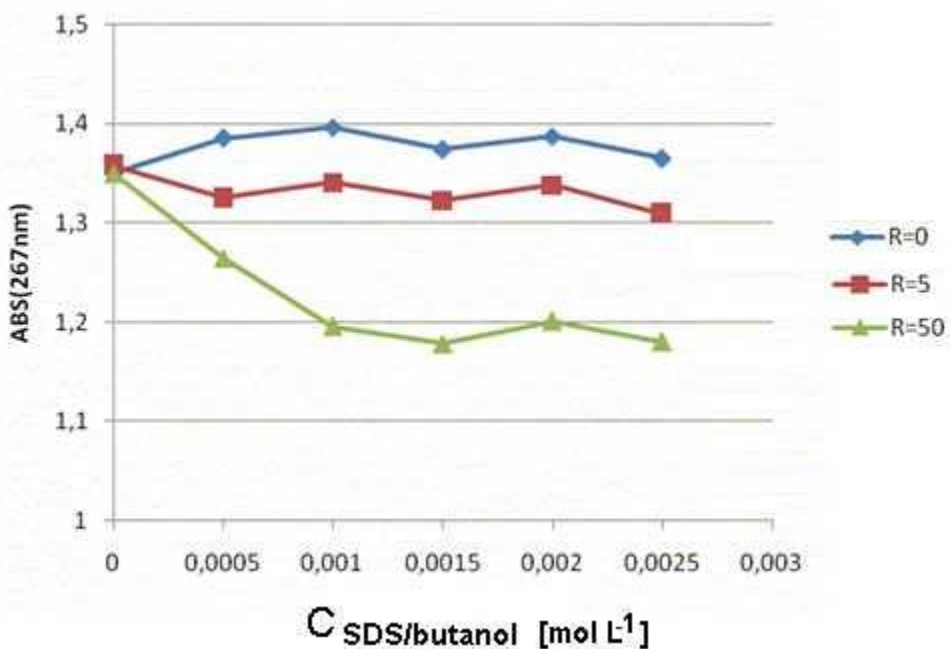


Figure 7: Absorption of thymidine band II at 267nm as function of SDS/heptanol concentration for different R.

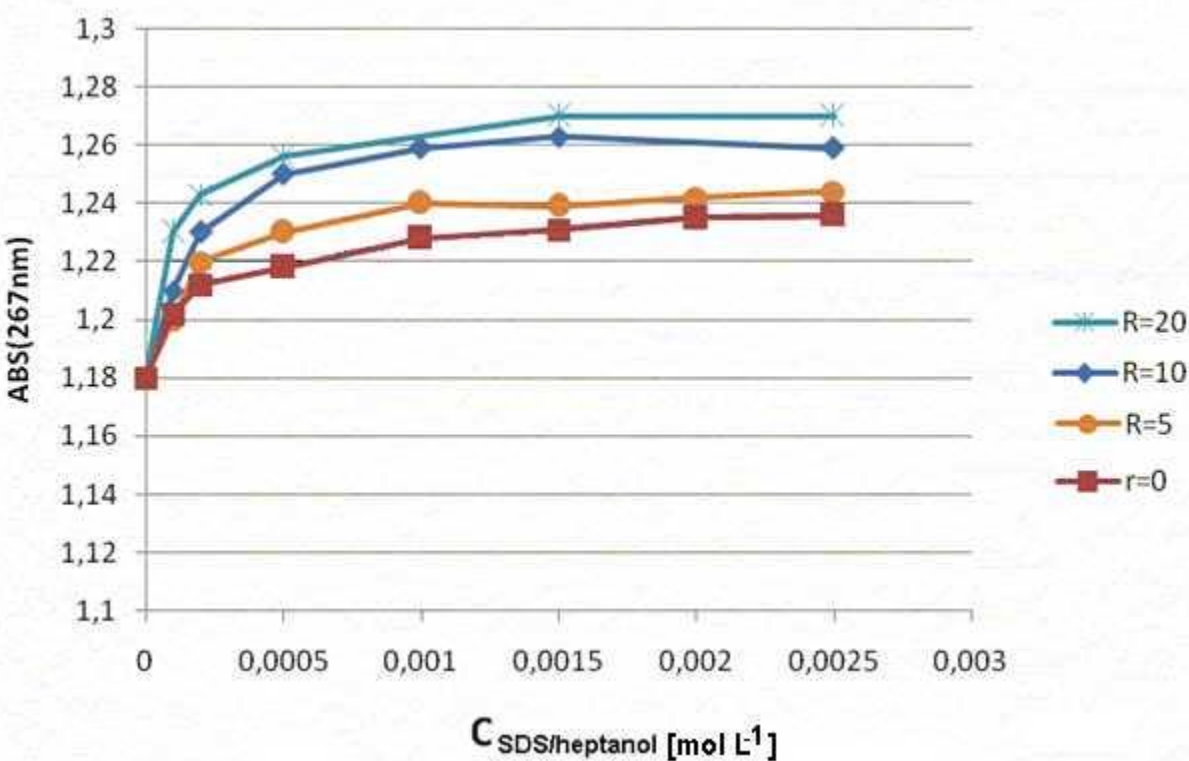


Figure 8: Absorption of thymidine band II at 267nm as function of SDS/decanol concentration for different R.

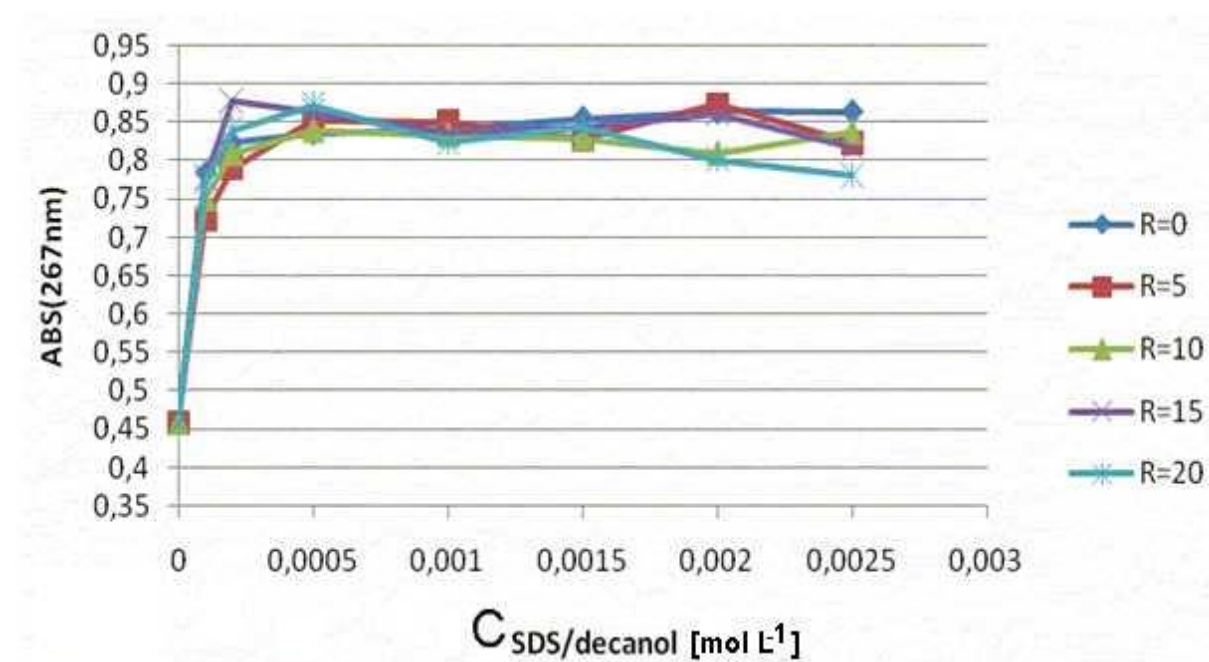


Figure 9: Binding constants of thymidine and SDS micelles as a function of hydrocarbon chain length in solvents with different water addition.

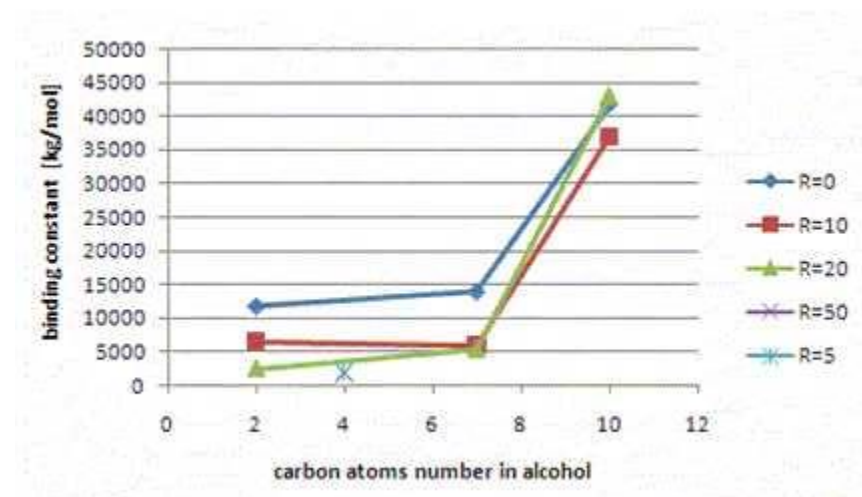
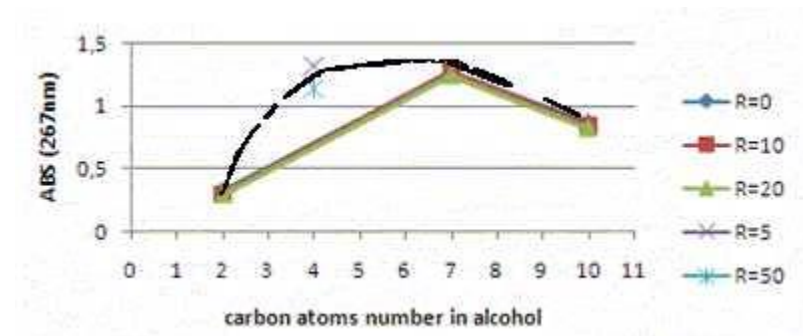


Figure 10: Thymidine absorption at micellar phase in alcohols in the water presence.**Table 1:** Critical micelle concentration (CMC for SDS in alcohols).

Number of carbon atoms in alcohol	CMC [mmol/L]
2	0.412
4	0.302
7	0.274
10	0.261

Table 2: The fitting parameters in the NLREG analysis of the UV-Vis data for thymidine partitioning between SDS micelles and alcohols for different R parameter ($R=[H_2O]/[AOT]$).

Alcohol	R	K' [kg/mol]	A_m	K
Ethanol	0	11700	0.3210	40.57
	10	6524	0.2980	22.62
	20	2511	0.2910	8.71
n-butanol	5	1915	1.3200	6.64
	50	1820	1.1400	6.31
n-heptanol	0	13867	1.2665	48.09
	10	6024	1.2697	20.89
	20	5370	1.2383	18.62
n-decanol	0	41600	0.8630	144.26
	10	37000	0.8430	128.31
	20	43100	0.8210	149.46