ROMANIAN ACADEMY

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INSTITUTE OF PHYSICAL CHEMISTRY

PhD THESIS SUMMARY:

Research regarding systems with surfactants and/or fluorophore-grafted polymers

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BUCHAREST
- 2017 -

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KEYWORDS: surfactant, fluorophore-grafted polymer, associative polymer, polymer-surfactant interaction, intramolecular aggregate, micellar solubilization, fluorescence, micellar electrokinetic chromatography, borax, reverse micelle, restricted nanoscopic environment

N.B.   In this summary the numbering of the figures, tables and chapters from the thesis was kept.

INTRODUCTION

Surfactants are compounds whose molecules are formed by both hydrophilic and hydrophobic parts. The existence of these antagonistic groups gives them special properties. Thus, surfactants adsorb on surfaces and interfaces, reducing surface and respectively interfacial tension. In addition, they aggregate when their concentration exceeds critical micelle concentration (CMC). Micellization of surfactants is influenced by many factors including the nature of the polar and non-polar groups, the addition of inorganic or organic electrolytes, of polar organic compounds [1] etc.

Associative polymers (PA) are a relatively new class of hydrophobically modified macromolecular compounds, with water solublility. They are able to associate by forming intra- and intermolecular aggregates [2]. The great variety of this class of polymers is due both to the diversity of the precursor polymers and to the multitude of compounds with which the grafting can be achieved [3].

Aqueous media interactions between PA and surfactants are a current topic and also an important chapter of polymer chemistry. These mixtures are used to modify viscosity and control rheology [4-6], stabilize colloidal systems [7], emulsify or flocculate [8] etc. In addition, PA-surfactant systems are used in cosmetics [9], drugs [10], paints [11], detergents, pesticides [1] etc.

What happens in associative polymer systems, in the absence or presence of additives, is easily tracked at a macroscopic level by means of colligative-based properties. It is, however, difficult to obtain information about the phenomena that occur at nanometric levels and how they are influenced by external stimuli. In addition, there are situations when the sample quantity is very small, making it impossible to apply methods that use large amounts of substance, such as viscozimetry, rheometry, NMR, etc.

A very good method in this situation is fluorescence. However, due to the fact that the hydrophobically modified polymers with alkyl chain are not fluorescent, its application is limited to the fluorescent probes. These give information about the polarity and microviscosity of the formed aggregates and highlight the onset of polymer-surfactant interaction. However, they do not provide data on the conformation of the polymer in solution, and how it reacts under the influence of external stimuli (pH, ionic strength, polar organic compounds etc.). To obtain such information, fluorophore grafted polymers are employed, such as polyacrylic acid grafted with 1-naphthylmethylamine and 1-pyrenemethylamine, used in this thesis.

This PhD thesis aims to obtain new information about the phenomena that occur in systems containing surfactants and/or polymers grafted with fluorophores in an aqueous medium, over time, and on the addition of inorganic salts, as well as in the water encapsulated in reverse micelles. This goal was achieved through the following objectives:

O_1.   **Evaluation of the effect of borax on sodium dodecyl sulfate (SDS) aggregation capacity,** using a polycyclic aromatic hydrocarbon (PAH), naphthalene, as micelle solubilisation probe.

O_2.   **Evaluation of the effect of borax on the complex formed between sodium dodecyl sulfate and poly(acrylic acid) ungrafted or grafted with 1-naphthylmethylamine.**

O_3.   **The temporal evolution of the association process between PAA25Np3 and dodecyltrimethylammonium chloride ($C_{12}TAC$).**

O_4.   **Evaluation of the behavior of poly(acrylic acid) grafted with 1-pyrenemethylamine in reverse micelles of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) at different degrees of hydration.**

The doctoral thesis consists of 9 chapters. **The first chapter** contains general theoretical aspects related to surfactants and polymers.

Chapter 2 contains two parts. The first is an introduction to associative and fluorophore-grafted polymers and their interactions with surfactants, and the second deals with the current research directions in this field.

In **Chapter 3** are stated the purpose and the objectives of the doctoral thesis.

Chapter 4 briefly describes the materials and methods used for investigation.

Chapters 5, 6, 7 and 8 constitute the original part of the thesis. **Chapter 5** assesses the effect of borax on the sodium dodecyl sulfate aggregation capacity, with consequences on micelle solubilization of naphthalene. **Chapter 6** presents a detailed study of the interaction in aqueous medium of a naphthalene labeled poly(acrylic acid) and the anionic surfactant with the most applications - sodium dodecyl sulfate. **Chapter 7** tackles in a rigorous manner the interaction between the same naphthalene-labeled polymer and the cationic surfactant - dodecyl trimethylammonium chloride. Because the polyelectrolyte and the surfactant used have opposite charges, a phase separation is produced in the pre-micellar region of the surfactant. The chapter also contains data on the influence of the preparation protocol of samples on the studied polymer-surfactant systems. **Chapter 8** describes the behavior of a poly(acrylic acid) grafted with different amounts of pyrene in the reverse micelles of sodium dioctyl sulfosuccinate at different degrees of hydration. The obtained data indicate new perspectives on fluorescent-labeled polymer interactions and its dynamics in nanoscopic aqueous media. **Chapter 9** contains the overall conclusions of the studies, the original contributions, the prospects for further research in this field and the dissemination of results. The paper ends with the bibliography employed in the thesis.

RESULTS AND DISCUSSION

4.2. Synthesis of poly(acrylic acid)s grafted with fluorophores

The grafting of the polymers was accomplished by random amidation of the carboxyl groups of the two above-mentioned poly(acrylic acids) with 1-naphthylmethylamine and 1-pyrenemethylamine. The solvent used was anhydrous N-methylpyrrolidone (NMP), and N,N'-dicyclohexylcarbodiimide (DCC) was used to remove traces of water. Finally, the following polymers were obtained:
- poly(acrylic acid) with molecular weight 25000 Da grafted with 3% mol. of 1-naphthylmethylamine (PAA25Np3),
- poly(acrylic acid) with molecular weight 150000 Da grafted with 3% mol. of 1-pyrenemethylamine (PAA150Py3), and
- poly(acrylic acid) with molecular weight 150000 Da grafted with 0.4% mol. of 1-pyrenemethylamine (PAA150Py0,4).

Their molecular structure is shown in **Figure 4.2**.
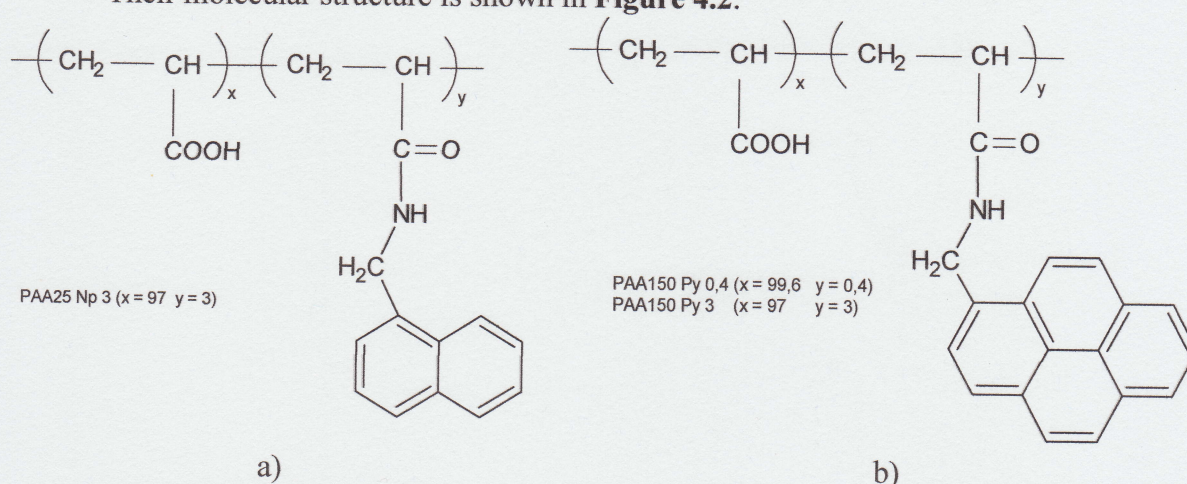
Figura 4.2. Chemical structures of the synthesized polymers a) PAA25Np3, b) PAA150Py0,4 şi PAA150Py3

5. Determination of the critical micelle concentration of sodium dodecyl sulfate by micelle solubilisation method

The results presented in this chapter are accepted for publication in ***Environmental Engineering and Management Journal (FI = 1,096).***

A promising and effective method for the removal of PAH from the environment is their solubilization in the surfactants' micelles [12,13]. However, not all surfactants are environmental friendly, many of them being particularly aggressive. Also, very important is the critical micelle concentration of the surfactant. The lower the CMC, the lower the amount of surfactant used for micellar solubilization. SDS is an environmentally friendly surfactant, whose CMC can be lowered in the presence of salts. Among inorganic salts, borax decreases the CMC more efficiently than uni-univalent or uni-bivalent electrolytes. In addition, it is widely used in cosmetics, biomedical, pharmaceutical, agricultural or industrial products [14-16]. These premises generated the idea of studying the SDS-borax mixture for the removal of condensed polycyclic aromatic hydrocarbons, considering naphthalene as model PAH.

Following micellar electrokinetic chromatography (MEKC) measurements, the effective electrophoretic mobility (μ_{eff}) of naphthalene (Np) was calculated. By plotting μ_{eff} versus the SDS concentration (see **Figure 5.1**) the CMC of the surfactant is obtained.
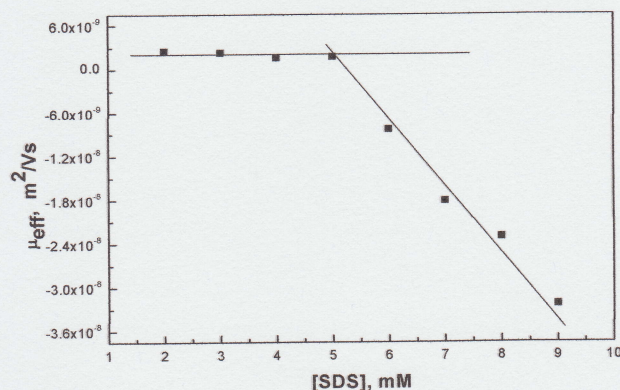
Figure 5.1. Effective electrophoretic mobility of naphthalene versus the concentration of SDS in 5 mM borax solution

The CMC value obtained by MEKC was confirmed by surface tension measurements and UV-Vis absorption. The results indicated an increase in probe solubility in the borax micellar system.

The solubilization capacity of the surfactant and the partition of Np between the micellar medium and water was determined spectrophotometrically in the absence and presence of borax. Using the solubility of naphthalene at a concentration above CMC (S_t), the solubility at CMC (S_0) and surfactant's concentration above CMC (C_t), the molar solubilization ratio (*MSR*) was calculated. This ratio is a measure of the efficiency of SDS micelles to solubilize polycyclic aromatic compounds, such as naphthalene, and is expressed in moles/moles.

Figure 5.4 shows the S_t-S_0 versus C_t-*CMC* curves for the solubility of Np in micellar systems. They show that, over the CMC, the amount of solute increases linearly with the surfactant concentration. It is also obvious that, in the presence of borax, the ability of SDS micelles to solubilize naphthalene is much greater.
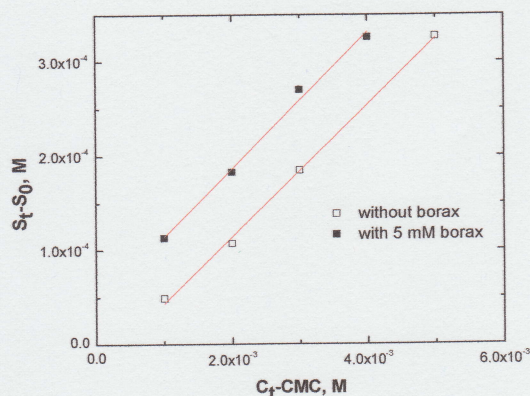
Figure 5.4. Solubilization of Np in SDS micelles in the absence and presence of 5 mM borax

MSR values were obtained from the slopes of the solubility curves, using the least square linear regression method. In the micellar system without borax, MSR is 0.070 and 0.073, respectively, with borax. The values are comparable to those found in literature.

6. Evaluation of the effect of borax upon the sodium dodecyl sulfate-grafted or ungrafted poly(acrylic acid) complex

The results presented in this chapter were published in *Colloid and Polymer Science, 294 (2016) 927-939 (FI = 1,723).*

Poly(acrylic acid) is a weak polyelectrolyte, responsive to numerous stimuli existing in solution. The addition of surfactant modifies the conformation of the polymer and produces the association with it. On the other hand, the presence of an inorganic salt in solution diminishes the electrostatic repulsions between the charged groups of the polyelectrolyte and the surfactant.

In this doctoral thesis chapter, the effect of borax upon the complexes formed between sodium dodecyl sulfate and poly(acrylic acid) was evaluated. In a first step, a poly(acrylic acid) (PAA) with molecular weight 25000 Da modified modified with 2.4% mol. 1-naphthylmethylamine (PAA25Np3) was synthesized, then was characterized by nuclear magnetic resonance, FT-IR and UV-Vis spectroscopy. Then, its interaction with SDS (both in the absence and in the presence of borax or sodium chloride) was investigated. The methods used were surface tension, electrical conductivity, UV-Vis spectroscopy, and static and dynamic fluorescence.

In this summary, only the steady-state fluorescence measurements for the ungrafted polymer will be shown, using pyrene (Py) as a fluorescence probe. This method can evaluate the number of hydrophobic domains formed between the polymer and the surfactant, as well as the impact of borax on them.

Pyrene is an aromatic compound with a very low water solubility of 6×10^{-7} M [17], capable of indicating the polarity of the micro-environment in which it is found [18]. By dividing the emission intensity of Py first vibrational peak (I_1) to the emission intensity of the third peak (I_3), and representing the variation of this ratio versus SDS concentration, one can obtain information about the polarity of the micro-environment around the Py probe. This ratio is called polarity index (PI).

Figure 6.4a shows the I_1/I_3 ratio versus SDS concentration in the absence and presence of the polymer and/or of salt. All curves have a typical sigmoidal pattern. A decrease of this ratio denotes a lower polarity and the localization of Py in a more hydrophobic micro-domain. It is known that PI has a value of about 1.8 in water, 1.2 in ethanol and 0.6 in aliphatic hydrocarbons [18]. At a low SDS concentration, the PI values are approximately 1.7, indicating that pyrene is located in water. By increasing the surfactant concentration, the I_1/I_3 values range from 1.1 to 1.3 suggesting the migration of the probe into the Stern layer of the SDS micelles, which has a polarity similar to that of ethanol. By comparing the I_1/I_3 values obtained by us in the concentration range of 4×10^{-3}-6×10^{-3} M SDS, it can be stated that Py is located in micro-media with different polarities. The complexation of PAA25 with SDS is affected by salt and is accompanied by increased hydrophobicity of the environment. This effect is related to an increase in the number of hydrophobic domains [19]. The sequence of polarity is as follows:

$$PI_{borax} < PI_{borax/poymer} < PI_{NaCl} < PI_{NaCl/polymer} < PI_{without\ polimer/salt}.$$

By dividing the intensity of the excimer's emission (I_E), centered at 470 nm, to the monomer's intensity (I_M), we obtained information about the ability of free Py monomers to form intermolecular excimers. The obtained I_E/I_M values for the studied systems are shown in **Figure 6.4b**. The I_E/I_M variation according to the SDS concentration is a typical micellar catalysis model for the excimer formation, where the Stern layer is considered the region in which the reaction takes place [20]. At low SDS concentrations, the I_E/I_M ratio is very low. By addition of SDS, several Py molecules are solubilized and concentrated in surfactant

clusters, as evidenced by the growth of I_E/I_M. The maximum value of the ratio shows that all Py molecules are solubilized in SDS aggregates. The further addition of SDS causes the distribution of Py across multiple SDS aggregates, which implies the decrease of the I_E/I_M ratio. The obtained results show that the system containing both polymer and NaCl creates the most efficient nano-containers capable of accumulating an optimal amount of Py. In the case of systems with surfactant, polymer and borax, the I_E/I_M maximum is low. This denotes smaller nano-structures of surfactant lower than those with NaCl.
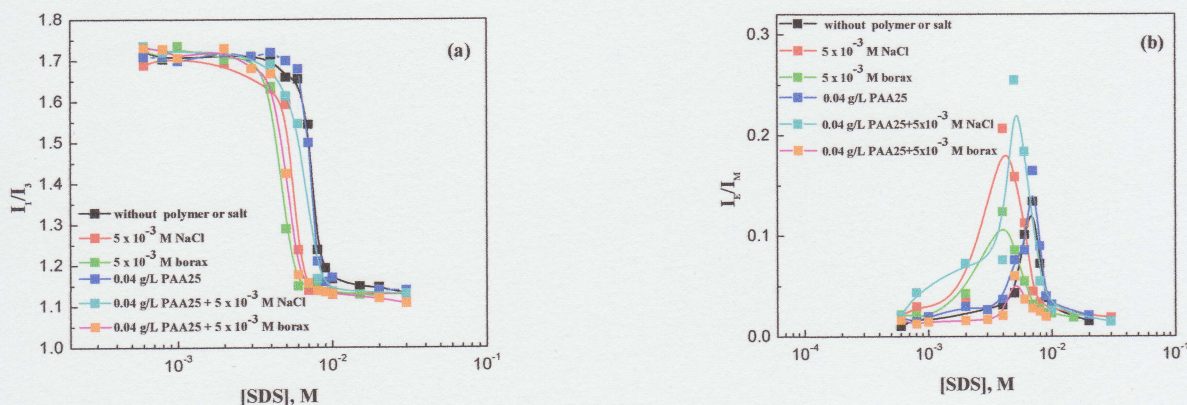

Figure. 6.4. Variation of I_1/I_3 (a) and I_E/I_M (b) of Py probe depending on SDS concentration in the absence and presence of 0.04 g/L PAA25, as well as inorganic electrolytes

7. Aging of surfactant-fluorescent polymer complex

The results presented in this chapter were published in *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 527 (2017) 81-88 (FI = 2,714).*

Electrostatic and hydrophobic interactions mainly control the association that occurs in solution between an opposite charge surfactant and a polymer, as well as the adsorption of the polymer-surfactant (PS) complex at air/water interface.

In this chapter was studied the behavior of PAA25Np3-C_{12}TAC aggregates, the colloidal stability of the system and the effect of the sample preparation procedure. For this purpose we used surface tension, pH, turbidity, electrophoretic mobility, dynamic light scattering (DLS) and static fluorescence.

In the literature, there is evidence that during mixing of the polyelectrolyte with the surfactant of opposite charge, kinetically stabilized aggregates are formed [21,22]. These entities stabilize due to the excess of polyelectrolyte or surfactant, and the steady state is reached after a very long time. To highlight these aggregates formed by mixing PAA25Np3 with C_{12}TAC, we performed DLS measurements. The left ordinate of **Figure 7.6** shows the average hydrodynamic radius (r_h) of the PAA25Np3-C_{12}TAC complex depending on the surfactant concentration and age of the sample and the right ordinate is the electrophoretic mobility. Between 3 x 10^{-5} M and 3 x 10^{-4} M C_{12}TAC, the r_h of the PS complex decreases with the surfactant concentration. For this concentrations range, the intensity of the scattered light and the turbidity index are very low. This suggests the formation of a small number of kinetically stabilized PS aggregates by the excess of PAA25Np3. Above 3 x 10^{-4} M C_{12}TAC, the PS complex increases because the cationic surfactant compensates for the negative loading of PAA25Np3. In excess of surfactant, there is a reversal of the electrical charge of the aggregates, their size decreases and finally becomes constant. DLS results demonstrate

that surfactants adsorb on the surface of the PAA25Np3-C_{12}TAC hydrophobic particles, forming a colloidal cluster dispersion of kinetically overloaded stabilized aggregates.
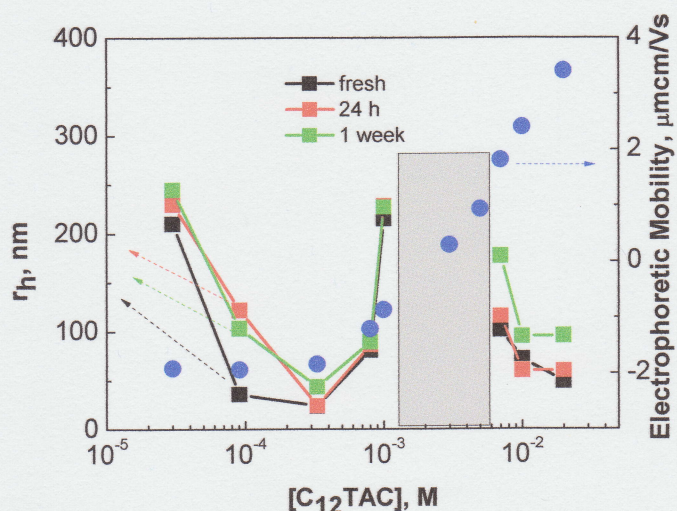

Figure 7.6. The hydrodynamic radius, r_h, (left ordinate) and electrophoretic mobility (right ordinate) of the PAA25Np3-C_{12}TAC complex versus surfactant concentration; the gray area indicates the phase separation region

In this study we used different ways to prepare the PAA25Np3 and C_{12}TAC mixture to demonstrate that in excess of surfactant, the PAA25Np3-C_{12}TAC complex forms a dynamically trapped entity.

Samples A, B and C were prepared as follows:
- from a stock of 0.8 g/L PAA25Np3 were taken 350 μL and added over the C_{12}TAC solution (sample A);
- from a stock of 0.4 g/L PAA25Np3 were taken 700 μL and added over the C_{12}TAC solution (sample B);
- C_{12}TAC was added slowly (6.3 mL/50 min) to the stock solution of 0.04 g/L PAA25Np3 with continuous stirring (sample C).

Table 7.1 shows the hydrodynamic radius, turbidity index, zeta potential and emission intensities of naphthalene's monomer and excimer for samples A, B and C subjected to the natural aging process. The final surfactant and polymer concentrations in these samples were 2 x 10^{-2} M C_{12}TAC and 0.04 g/L PAA25Np3.

Table 7.1. Hydrodynamic radius (r_h), turbidity index ($100-T_{400}$), ζ potential, I_M and I_E for samples A, B and C

Sample / Aging time	r_h, nm	$100-T_{400}$, %	ζ potential, mV	I_M, a.u.	I_E, a.u.
A/fresh	33	2	+41	18,6	3,4
A/24 h	43	5	+42	17,5	3,2
A/1 week	52	11	+42	15,4	2,9
A/2 weeks	65	14	+39	14,9	2,8
B/ fresh	49	15	+40	18,1	3,3
B/24 h	60	22	+42	16,6	3,0
B/1 week	96	21	+43	15,4	2,9
B/2 week	69	18	+40	15,6	2,9
C/ fresh	68	20	+38	16,3	3,0
C/24 h	81	30	+44	16,2	2,9
C/1 week	89	31	+41	15,7	2,8
C/2 weeks	94	32	+40	15,6	2,8

The DLS results indicate that in excess of $C_{12}TAC$, PAA25Np3 forms kinetically captured PS aggregates whose size depends on the concentration gradient present during mixing. After one week, an increase in the size of the PAA25Np3-$C_{12}TAC$ aggregates for all samples was noted, but the PS aggregates were higher when the addition of the surfactant solution in the aqueous polymer solution was slow. The fact that all the measured electrochemical potentials are positive proves that the aggregates are stabilized by excess of positive charges due to surfactant ions adsorbed on them. Changes in the size of the PAA25Np3-$C_{12}TAC$ complexes are corroborated by the increase in the turbidity index and the decrease in the emission intensity of naphthalene's monomer and excimer. A decrease in the size of PS aggregate occurs for sample B after two weeks, when the system becomes clearer according to turbidity data. These results demonstrate that over time, the properties of the solutions are affected by the preparation method and the addition order of components.

8. Self-aggregation of poly(acrylic acid) grafted with 1-pyrenemethylamine in crowded nanoscopic environments

The results presented in this chapter were published in *Journal of Photochemistry and Photobiology A: Chemistry, 328 (2016) 33-41 (FI = 2,625).*

To accomplish the fourth objective of the PhD thesis, two new poly(acrylic acid) samples with molecular weight 150000 Da grafted with 0.4% and 3% mol. of 1-pyrenemethylamine were synthesized. They were characterized by NMR, FT-IR spectroscopy and UV-Vis absorption. Then, the dynamics of these two polymers was monitored in the restricted aqueous medium provided by the AOT reverse micelles (RM) at different degrees of hydration (w_0). The investigation methods used were UV-Vis spectrometry, dynamic light scattering and stady-state and dynamic fluorescence.

Absorption spectra of PAA150Py3 in AOT reverse micelles are shown in **Figure 8.1a**. For comparison, the absorption spectrum of PAA150Py3 in water is also presented.

a)   b)
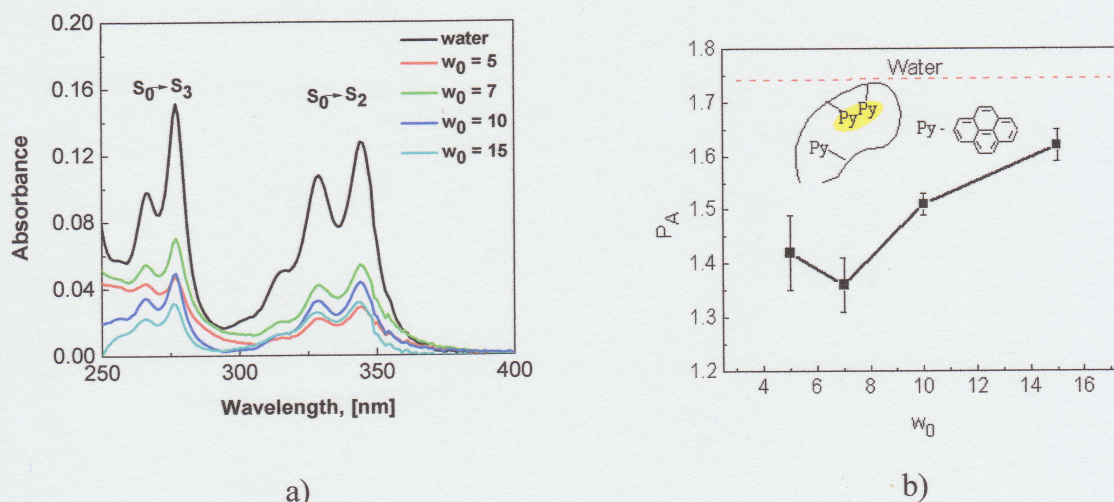
Figure 8.1. The absorption spectra of PAA150Py3 (a) and the dependence of P_A parameter of w_0 (b) in RM and in water

It is noted that the absorption spectra of PAA150Py3 in RM are different from those in water. The first show weaker transitions $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ than in water. **Figure 8.1a** shows that the absorbance of PAA150Py3 at 344 nm depends on w_0. This behavior occurs due to the concentration and subsequent dilution phenomenon of the polymer within the RM.

At 344 nm and $w_0 = 5$, absorbance is lower than in RM with higher water content. This shows that not all PAA150Py3 molecules are incorporated inside the small RM. When $w_0 = 7$, the absorption maximum increases and suggests an improved solubilization of the polymer within the RM. The further addition of water dilutes the amount of solubilized PAA150Py3 and the absorption signal decreases. The $S_0 \rightarrow S_2$ transition is used to evaluate the P_A parameter from the peak to valley absorption ratio between 300 and 400 nm. This parameter estimates the association level of the Py grafts prior to excitation. **Figure 8.1b** shows the P_A variation with the degree of hydration of the reversed micelles. It can be seen that P_A depends on the degree of hydration and has a minimum at $w_0 = 7$. In water, P_A equals 1.74, and in RM it is between 1.4 and 1.5 depending on the degree of hydration. The grafted PAA behavior can be evaluated by considering the photophysical response of Py to the intramolecular interactions that are established between the segments of the polymer coil. These interactions occur if the adjacent grafts are not separated or are separated by a small number of carboxyl groups. In PAA150Py3, approximately 32 acrylic units monomer correspond to one Py and the grafts are randomly distributed. When half of the carboxyl groups are dissociated, the pKa of PAA150Py3 is 4.5. In the study of this thesis, all experiments were performed at pH = 3.4 to prevent electrostatic repulsions between the surfactant and the polymer. At this pH, the PAA150Py3 behavior is very poorly affected by electrostatic repulsions because it has few dissociated carboxyl groups and adopts a compact conformation [23].

On the other hand, a water-soluble polymer labeled with pyrene has in a aqueous solution a $P_A < 3$, due to the association of the pirene grafts [24,25]. In **Figure 8.1b**, all P_A values are less than 3 and satisfy the Winnik condition. This suggests that in the aqueous nucleus of RM, Py aggregates predominately in fundamental state. The lowest P_A value occurs at $w_0 = 7$ and denotes the existence of a larger number of overlapped pyrene grafts than for other degrees of hydration. At this degree of hydration, the polymer is constrained in RM water, favoring multiple π-π interactions, and the aromatic units are closer to one another (at ~ 3 Å) [24].

Final conclusions

The research carried out within this doctoral thesis demonstrated the full accomplishment of all the proposed objectives. The conclusions reached are as follows:

• The ability of sodium dodecyl sulfate to solubilize PAH increases in the presence of borax. This means lower amounts of surfactant for the removal of polycylic aromatic hydrocarbons from polluted water.
• Borax lowers the critical micelle concentration of sodium dodecyl sulfate more effectively than sodium chloride. It also decreases the concentration at which a surfactant is aggregated on the polymer, called critical aggregation concentration (CAC).
• Addition of borax in PS systems results in increased pH, the unfolding of the polymer coil, and the stiffening of its segments.
• Fluorescent grafts and inorganic salts increase the adsorption capacity of the surfactants at the water/air interface and reduce the mobility of the counterions in the solution.
• The fluorescence data show that addition of surfactant decreases the self-aggregation of fluorescent grafts due to formation of the surfactant-graft complex, which leads to the unfolding of the polymer coil.
• In the case of polymer-surfactant systems of opposite charges, the measurements carried out showed the presence of kinetically stabilized PS aggregates with positive or negative charges - depending on the excess component (polymer or surfactant). The

formation of these aggregates and their temporal evolution depend on the manner in which samples are prepared. Higher PS aggregates are obtained when the surfactant solution is added gradually to the polymer solution.

- The fluorescent grafts self-assemble differently in the encapsulated RM water compared to the way they do it in a common aqueous solution.
- In the water inside the large RM, hydrogen bonds were shown similar to those present in ordinary water.

Original contributions

The research carried out within this doctoral thesis is in line with the proposed objectives. It is original and has scientific value confirmed by its publication in specialized journals in colloids field. The originality elements are as follows:

- Two new associative polymer specimens were obtained, fluorophore-labeled, exhibiting physico-chemical properties different from those of the precursor polymers.
- A comparison of the solubilization capacity of an aromatic compound in the direct sodium dodecyl sulfate micelles was made in the presence of two inorganic salts: borax and sodium chloride.
- Micellar electrokinetic chromatography was correlated with common techniques for critical micelle concentration determination, such as surface tension, UV-Vis absorption and steady-state fluorescence.
- The effect of borax on the fluorophore grafted polymer-surfactant systems was studied for the first time and its superior stabilizing capacity compared to that of sodium chloride was demonstrated.
- Also for the first time, the time effect on the fluorophore-grafted polymer-surfactant system of opposite charges was analyzed in a systematic manner.
- New aspects of the encapsulation of poly(acrylic acid) grafted with pyrene in reverse surfactant micelles have been highlighted.
- Research has shown the strength and type of interactions that take place in the associative polymer-surfactant systems with and without inorganic electrolyte.
- By controlling the concentration and architecture of associative polymers, ionic strength, the additive added, and sample preparation protocol, useful nanomaterials in various applications can be obtained.

Dissemination of results

Results dissemination of the doctoral thesis was made in a number of four ISI articles, three oral presentations and three posters held at international and national conferences.

List of published ISI papers regarding the subject of the PhD thesis

1. Ageing of fluorescent and smart naphthalene labeled poly(acrylic acid)/cationic surfactant complex, **E.L. Simion**, G. Stîngă, A. Iovescu, A. Băran, D.F. Anghel, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 527(2017), 81-88 (F.I. = 2,714);

2. Self aggregation of pyrene labeled poly(acrylic acid) in nanoscopically crowded environments, G. Stîngă, A. Băran, A. Iovescu, **E.L. Simion,** L. Aricov, D.F. Anghel, *Journal of Photochemistry and Photobiology A: Chemistry*, 328 (2016), 33-41 (F.I. = 2,625).

3. Smart borax complexes starting from anionic surfactant in association with unlabeled or fluorescently labeled poly(acrylic acid)s, **E.L. Simion**, G. Stîngă, A. Băran, L. Aricov, I.C. Gîfu, D.F. Anghel, *Colloid and Polymer Science*, 294 (2016), 927-939 (F.I. = 1,723);

4. A micellar decontamination strategy for of polycyclic aromatic hydrocarbons from environment, **E.L. Vasilescu**, M. Balcan, G. Stîngă, A. Băran, I.C. Văcăreşteanu, L. Aricov, D.F. Anghel, accepted for publication in *Environmental Engineering and Management Journal* (F.I. = 1,096);

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