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“*ILIE MURGULESCU*” INSTITUTE OF PHYSICAL CHEMISTRY

PhD THESIS SUMMARY:

THE STUDY OF PHYSICOCHEMICAL PROPERTIES OF HYDROPHOBICALLY MODIFIED POLYMERS IN AQUEOUS MEDIUM

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Summary

PART 1
THEORETICAL CONSIDERATIONS

PART 2
ORIGINAL RESULTS

Keywords: hydrophobically modified polyacrylates; intramolecular aggregates; intermolecular aggregates; fluorescence spectroscopy; dynamic rheology; adsorption at the solution/air interface; thin liquid films of polymer; polymer-surfactant systems; fluorescent probes solubilization.

1. Introduction

An important class of polymers that has aroused great interest in the last decades is that of the water soluble associative polymers (PA), also called hydrophobically modified polymers (PMH). The structure of these amphiphilic macromolecular compounds is constituted by a hydrophilic backbone on which is grafted some hydrophobic side groups. This leads to obtain unique materials, which are useful in a variety of applications. The structure and stability of PMH is given by the interplay of repulsion and attraction forces, where the hydrophobic interaction plays a very important role, because the nonpolar groups repel the water molecules and tend to assemble in the surface layer of the aqueous solution, while the hydrophilic chain interacts with the water [1, 2]. By increasing the PMH concentration, the hydrophobic chains self-associate through intermolecular hydrophobic attractions and form specific hydrophobic aggregates. Intensive study of these materials is justified by the various areas in which they are used. PMHs have special properties, such as spectacular increase of viscosity [3], gelation [4], increase of elasticity [5] etc. Therefore, PMH are widely used in personal care products, cosmetics [6], carriers for proteins, DNA and drugs [7–12], waterborne paints [13, 14], wastewater purification [15], enhanced oil recovery [16–19], etc.

In this PhD thesis we have proposed to investigate the physicochemical properties of hydrophobic modified polyacrylates ($NaPAC_n$) in aqueous solution, addressing the following objectives:

- **The $NaPAC_n$ synthesis** by grafting method of polyacrylic acid (PAA) with linear fatty amines having an alkyl chain composed of 10 to 18 carbon atoms;
- **The characterization** of synthesized polymers by FT-IR and NMR spectroscopy;
- **The study of physicochemical properties** of $NaPAC_n$ using viscosimetry, dynamic rheology, steady-state and dynamic fluorescence, and refractometry;
- **The determination of viscoelastic behavior** of associative polyacrylates at different concentrations, in the absence or presence of an electrolyte (NaCl) and at different pH values;
- **The characterization of solution/air interfacial adsorption layers** of the $PAAC_n$ by tensiometric analysis on the contour of an air bubble from inside the polymer solution. The resulted measurements will help us to determine both the equilibrium surface tensione (σ_{ech}) and the rheological behavior of surface dilational (surface dilational elasticity and viscosity);

- **The analysis of polymer thin liquid films** by microinterferometry using Scheludko-Exerowa method. The obtained data will contain information about the drainage, homogeneity, thickness and stability of the polymer film;
- **The investigation of the surfactants effect** on $NaPAC_n$. The chosen surfactants are of different classes (nonionic, anionic and cationic) and have the same hydrophobic chain length. The study will be done by characteristics methods used for amphiphilic materials (surface tension, viscosity), and by complementary methods (pH, dynamic light scattering). The results will help us to detect the critical micellar concentration (CMC) and critical aggregation concentration (CAC), and to highlight the type and strength of the interactions between the system components;
- **The assessment of the solubilization capacity** of fluorescent probes in surfactant-polymer systems using steady-state and dynamic fluorescence. We will use two probes, one hydrophobic (pyrene) and one less hydrophobic (3-methoxybenzantrone – MBA). The pyrene behavior in polymer-surfactant systems is somewhat known – but not fully elucidated, data on the solubilization of the MBA in such systems are inexistent. The obtained results will help us to find out if the polymer improves the solubilization capacity of the surfactant.

The present PhD thesis has **two parts** and **eight chapters**. The first part consists of two chapters. In **Chapter 1** is presented the theoretical considerations regarding water-soluble associative polymers, the general characteristics of hydrophobic modified polyacrylates and the influence of surfactants on unmodified and modified polyacrylates in aqueous solution. Also in the first chapter are mentioned the purpose and the objectives of the thesis. **Chapter 2** describes the used materials and their provenance, the sample preparation and the experimental methods.

The second part contains the original contributions of the thesis and has six chapters. Thus, **Chapter 3** comprises the analysis of polyacrylic acid (the precursor) by size-exclusion chromatography (SEC) and the synthesis method of hydrophobic modified polyacrylates.

The molecular structure of the synthesized polyacrylates, as well as their grafting and association degrees were determined using spectroscopic methods (FT-IR and NMR), and the results obtained are presented in **Chapter 4**.

Chapter 5 includes an extensive study on the aggregation of polyacrylates in aqueous solution using viscosimetry, dynamic rheology, steady state and dynamic fluorescence, and refractometry, specific methods to associative polymers.

Chapter 6 presents data on the behavior of hydrophobically modified polyacrylates in bulk and at solution/air interface. The study investigates the viscoelastic behavior of hydrophobically modified polymers with short hydrophobic chain (C_{10} and C_{12}). Also, in this chapter is investigated the characteristics of the thin liquid films formed by these polyacrylates.

Chapter 7 includes a complex study regarding the impact of surfactants on hydrophobically modified polyacrylates [$NaPAC_n$ ($n = 10$ and 18)], PAA and NaPA, using typical characterization methods of these systems (superficial tension and viscosity), but also complementary methods (pH, dynamic light scattering). Information on the solubility capacity of fluorescent probes in the investigated systems is obtained by steady state and dynamic fluorescence measurements using pyrene and 3-methoxybenzantrone (MBA) as the probes.

The final conclusions reached in this PhD thesis are presented in **Chapter 8**.

Experimental results and discussions

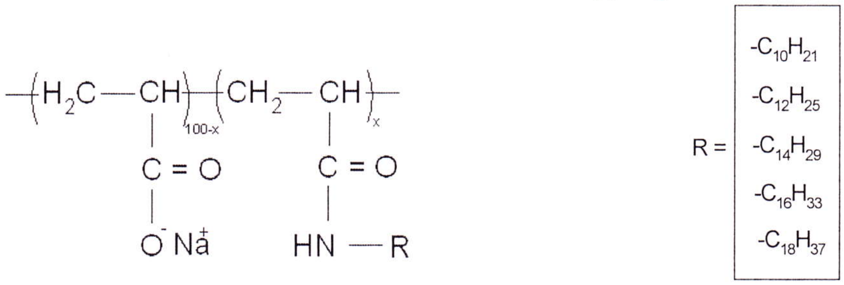
3. Synthesis of hydrophobically modified polyacrylates

The results are published in **Colloid and Polymer Science (2016) 294: 667-679.**

Water-soluble hydrophobically modified polyacrylates ($NaPAC_n$) were synthesized by grafting the polyacrylic acid with linear fatty amines ($n = 10$, 12, 14, 16 and 18).

The modification of polyacrylic acid was made by reacting the alkylamine with the carboxyl group of PAA at 60 ° C in the presence of N,N'-dicyclohexylcarbodiimide (DCC) using 1-methyl-2-pyrrolidone (MPD) as a solvent [20]. The PAA modified was neutralized and precipitated in NaOH (40 %). The synthesized polymers were purified by dialysis and recovered by lyophilization.

Scheme 1. Molecular structure of $NaPAC_n$ (x = grafted amount).



Finally, five hydrophobically modified polymers having a theoretical grafting degree of 3% (mole) were obtained. The molecular structure of $NaPAC_n$ is illustrated in **Scheme 1**.

4. Chemical composition evaluation of hydrophobically modified polyacrylates

The results are published in **Colloid and Polymer Science (2016) 294: 667-679.**

The chemical composition of $NaPAC_n$ was evaluated by FT-IR and ^{1}H-NMR spectroscopy. The obtained results have shown that PAA amidation has been successful made. Additionally, ^{1}H-NMR spectroscopy gives quantitative information regarding the modification degree of PAA. As can be seen from **Table 1**, the grafted amount calculated from ^{1}H-NMR spectra were smaller than 3% (molar). This behavior can be attributed to the lower reactivity of fatty amines [21].

Table 1. Grafted amount (x) of $NaPAC_n$ calculated from ^{1}H-NMR spectra.

Polymer	**x, [%, molar]**
$NaPAC_{10}$	2,90
$NaPAC_{12}$	2,80
$NaPAC_{14}$	1,60
$NaPAC_{16}$	2,60
$NaPAC_{18}$	2,30

5. The investigation of aqueous solutions of NaPA and $NaPAC_n$

The results are published in **Colloid and Polymer Science (2016) 294: 667-679.**

Although hydrophobic modified polyacrylates have been extensively studied around the '90s of the last century, their behavior in aqueous solution is not yet fully understood. So, there are many lacunas in how they associate in solution, and the researches perfomed within this PhD thesis are focused on their elucidation.

The $NaPAC_n$ aqueous solution behavior was investigated by viscosimetry, dynamic rheology, steady-state and dynamic fluorescence (using piren as probe) and refractometry.

The obtained results showed that $NaPAC_n$s in dilute regim have low viscosity, but at high concentrations, above the concentration at which intermolecular aggregates (c*) occur, the viscosity increases sharply (see **Figure 1**). The parameter c* (determined by Newton's method) decreases with increasing the hydrophobic chain length as witnessed by the values in **Table 2**.

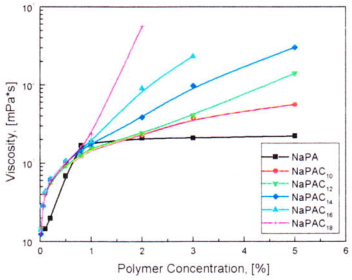


Fig. 1. Viscosity modification with polymer concentration at 23° C.

Table 2. c* values for NaPAC$_n$

Polymer	**c*, [%]**
NaPAC$_{10}$	1,43
NaPAC$_{12}$	1,32
NaPAC$_{14}$	0,89
NaPAC$_{16}$	0,71
NaPAC$_{18}$	0,67

The steady-state fluorescence measurements have shown that, unlike NaPA aqueous solutions, the NaPAC$_n$ forms intramolecular hydrophobic microdomains, a phenomenon marked by the decrease of pyrene polarity index (I_1/I_3). Intramolecular microdomains occur at a concentration that depends on the alkyl chain length and the grafting degree of the polymer.

Worthy to mention is that the refractive indices allowed to detect both intramolecular (**Figure 2**) and intermolecular (**Figure 3**) association.

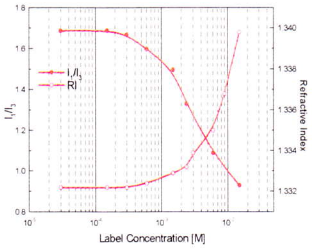


Fig. 2. The comparison of polarity index and refractive index variation with label concentration for NaPAC$_{10}$.

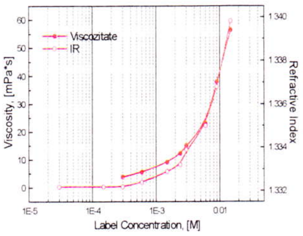


Fig. 3. The comparison of viscosity and refractive index variation with label concentration for NaPAC$_{10}$.

The hydrophobic modified polyacrylates obtained in this doctoral thesis were also characterized in terms of viscoelastic behavior. The measurements were perfomed at 3 % (wt.) polymer concentration. The obtained viscoelastic responses were as it follows: For NaPAC$_{10}$, NaPAC$_{12}$, and NaPAC$_{14}$, the elastic component (G') was smaller than the viscous component (G") – G' < G", meaning that the polymer aqueous solutions have fluid character. The behavior of NaPAC$_{16}$ and NaPAC$_{18}$ is exactly the opposite, namely G' > G", highlighting a solid character. The NaPAC$_n$ viscoelastic behavior is supported by both dynamic yield stress and relaxation times of the polymers.

6. The behavior of hydrophobically modified polyacrylates in bulk and at solution/air interface

The results are published in **Colloids and Surfaces A: Physicochemical and Engineering Aspects (2016) 505:138–149.**

The study presented in this chapter includes systematic investigations of the $PAAC_{10}$ and $PAAC_{12}$ properties in bulk and at solution/air interface. The emphasis is on the balance between hydrophobic interactions (intra- and inter-molecular) and electrostatic interactions, as well as on how this equilibrium is affected by external stimuli (pH and ionic strength).

The properties and characteristics of hydrophobic modified polyacrylates in bulk and at solution/air interface indicate that their performance depends on the pH, and in a lesser extent to the presence of an inorganic electrolyte and the length of the hydrophobic alkyl chain.

The effect of pH significantly changes the viscoelastic properties of the studied polymers. By increasing the pH, the polymer conformation changes from a static compact chain (acidic pH) to a rigid and uncoiled chain (basic pH). Thus, the viscoelastic response of $PAAC_{10}$ solutions at acidic and basic pH, in the absence or presence of the electrolyte, is that of a viscous liquid. Interestingly is that at neutral pH (regardless the NaCl presence) the viscoelastic response is that of a elastic solid, behavior given by the interplay between the hydrophobic and electrostatic interactions which favor the formation of intermolecular networks. The $PAAC_{12}$ aqueous solutions, without or with electrolyte, at the same pH value exhibit a viscoelastic response identical to that found in the case of the polymer with shorter hydrophobic chain. The difference is made by the rheological modules values, which are lower in the case of the grafted polymer with longer alkyl chain. This proves that the $PAAC_{12}$ forms easier and more compact intramolecular aggregates than $PAAC_{10}$.

The dynamic tensiometric results confirm that the pH modification has a major effect on the polymers aqueous solution properties and the presence of inorganic electrolyte affects the competition between the electrostatic and the hydrophobic interactions, which leads to modification of the polymer chain conformation. Thus, the equilibrium surface tension (σ_{eq}) decreases with the pH lowering. At acidic pH, the lowest σ_{eq} value was recorded, so the acidic polymer can be considered a polymer surfactant. The differences that occur due to the increase of the hydrophobic alkyl chain length are as follows: (a) $PAAC_{12}$ reaches harder the σ_{eq} than $PAAC_{10}$; (b) at acidic pH, σ_{eq} has higher values for $PAAC_{12}$ and the addition of NaCl increases the solution hydrophobicity, unlike $PAAC_{10}$ where the presence of the electrolyte has an opposite effect; (c) at alkaline pH, the polymer with longer alkyl chain is more hydrophobic (σ_{eq} is lower) and the salt presence increases the hydrophobicity of the studied polymers.

Another method used to investigate the adsorption layers at the solution/air interface formed by hydrophobic modified polymers was surface dilatational rheology. The obtained results demonstrate the effect of pH and inorganic electrolyte on the superficial properties of $PAAC_n$ solutions. Thus, the electrolyte presence is beneficial at alkaline pH because it increases the hydrophobicity, the surface elasticity and viscosity of the system. All are due to screening effect of electrostatic repulsion by the electrolyte. Instead, at acidic pH, the NaCl addition decreases the surface elasticity, but does not significantly change the system hydrophobicity. Comparing the data obtained for $PAAC_{10}$ and $PAAC_{12}$ solutions without salt, it was noted that the $PAAC_{12}$ has higher surface elasticity and viscosity, leading to the same conclusion: the longer hydrophobic grafts tend to associate intramolecularly more easy. However, the salt impact on the surface properties of the studied polymers is rather complicated and does not depend on the concentration or the length of the alkyl chain grafted hydrophobic polymer.

The microscopic study performed on thin liquid films of $PAAC_n$ validates the previously obtained results regarding the competition between hydrophobic and repulsive forces.

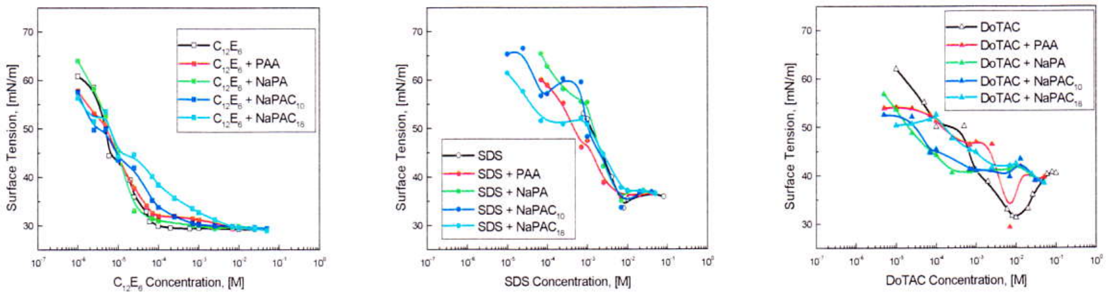
7. The effect of surfactants on PAA, NaPA and $NaPAC_n$

The results are published in **Colloid and Polymer Science (2017)**
DOI:10.1007/s00396-017-4102-0

There are many studies in the literature on the interaction between surfactants and polymers, but very few on the effect of surfactants on the hydrophobically modified polyacrylates. In addition, there is no systematic study on the interaction of different types of surfactants and $NaPAC_n$ in a dilute regime. These are the reasons why, in the present study, we firstly investigated the interactions of surfactants with $NaPAC_n$ (n = 10 and 18), comparing them with those of the same surfactants with PAA or NaPA. The used surfactants were hexaethylene glycol monododecyl ether ($C_{12}E_6$), sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DoTAC). The study was done using the following methods: surface tension, viscosity, pH, DLS, steady-state and dynamic fluorescence. Pyrene (hydrophobic) and 3-methoxy-7H-benzo[de]anthracen-7-one (MBA – less hydrophobic) were used as fluorescent probes. The polymer concentration was kept constant at 0.1% (wt.).

The results showed that, at low surfactant concentrations (irrespective of its nature) the systems behavior is given by the polymer and at high concentrations, the behavior is dictated by the appearance of free micelles. The CAC is characteristic of each studied surfactant-polymer system, because both hydrophobic and electrostatic forces participate in the complex formation.

In $C_{12}E_6$-polymer systems, the aggregates formation is dictated by hydrogen bonds and less, by hydrophobic interactions. This is way, the $C_{12}E_6$-PAA and $C_{12}E_6$-NaPAC$_n$ systems had the lowest CAC (see **Figure 4A**). The SDS impact on polymers is more evident in the presence of NaPAC$_{18}$ (even if the system components have the same electrical charge), due to its ability to self-associate (see **Figure 4B**). The DoTAC interacts electrostatically – mainly – with all anionic polymers, but most strongly with NaPA (see **Figure 4C**).



A B C

Fig. 4. Surface tension isotherms for the investigated systems.

The study on the solubilization of pyrene and MBA in the surfactant-polymer systems has shown that the fluorescent probes are solubilized in three kinds of hydrophobic microenvironment: into the surfactant micelles, the intracoil microdomains of the NaPAC$_n$, and the surfactant–polymer complex. The fluorescence data revealed that the probes solubilize in the micellar palisade layer, their lifetime and/or fluorescence intensity being higher in these protected media. Generally, in the studied systems, the probes lifetimes increase due to their solubilization in a more appropriate microenvironment which protects the probe against the oxygen quenching.

In the $C_{12}E_6$-polymer complexes, the MBA has the lowest emission intensities and the shortest lifetimes due to the competition between the probe and the nonionic surfactant to form H-bonds with the polymers, especially with PAA. Instead, in mixtures with NaPAC$_{18}$, the MBA exhibits the longest lifetime and highest emission intensities because it is located in the polymer intramolecular domains and in polymer bound micelles.

It is important to mention that the impurities of ionic surfactants interact with the chemical species present in the system.

8. Final conclusions

- Five hydrophobically modified polyacrylates were obtained by grafting PAA with *n*-alkyl amines. PAA amidation was demonstrated by FT-IR and ^{1}H-NMR spectroscopy, and the NaPAC$_n$ grafted degrees were below 3% (mol);
- NaPAC$_n$ forms in water intra- and inter-molecular hydrophobic microdomains. In general, the formation of intramolecular microdomain depends on the grafting degree and the intermolecular ones on the hydrophobic chain length;
- The viscoelastic behavior of the NaPAC$_{10}$, NaPAC$_{12}$ şi NaPAC$_{14}$ was liquid like ($G' < G''$); In contrast, NaPAC$_{16}$ and NaPAC$_{18}$ have a strong solid viscoelastic character ($G' > G''$);
- The properties and characteristics of the NaPAC$_n$, in bulk and at solution/aer interface, indicate that the performance of the these polymers depend on both pH and inorganic electrolyte quantity, and change in a systematic way with the increase of the alkyl graft length;
- The studies on polymer liquid films validate the interplay of hydrophobic and electrostatic interactions;
- The CAC occurrence depended on each surfactant due to the reciprocal action of hydrophobic and electrostatic forces. Thus, the C$_{12}$E$_6$ interacts most strongly with PAA; the SDS effect was more evident on the NaPAC$_{18}$; in DoTAC case, the NaPA system shows the most significant interaction;
- The study on hosting properties of polyacrylate–surfactant complexes revealed that the fluorescent probes are solubilized in three kinds of hydrophobic microenvironments: into the surfactant micelles, the intracoil microdomains of the NaPAC$_n$, and the surfactant–polymer complex;
- The fluorescence data showed that the pyrene and MBA are located in the micellar palisade layer;

In conclusion, the aim of the PhD thesis was achieved by fulfilling all the objectives proposed.

Original contributions

The research done within this doctoral thesis is original and in accordance with the proposed scientific objectives. The original contributions brought by the present thesis have many novelties with a certain scientific value in the field of water-soluble associative polymers. They are the followings:

- A new class of compounds was obtained, the **hydrophobic modified polyacrylates**, with properties totally different from those of the poly(acrylic acid) precursor;
- The study regarding the behavior of hydrophobically modified polyacrylates in aqueous solution, made by a variety of methods, has shown that it is possible **to tailor materials with suitable characteristics for target applications**;
- **The refractometric method** was used **for the first time** in the literature to characterize the hydrophobic modified polyacrylates. This simple, accurate, and fast method requires small amounts of sample. It is capable of detecting **the two types of polymeric self-association (intra- and intermolecular)**;
- **The behavior** of hydrophobically modified polyacrylates in bulk and at solution/air interface **depends on the polymer nature**, the **pH** and the **presence of a low molecular weight electrolyte**;
- **The thin liquid films** of hydrophobic modified polyacrylate films, **studied for the first time**, **provide** information on the **flow**, **homogeneity**, **thickness** and **stability of the polymer film;**
- The researches on **the aggregation of polyacrylate-surfactant systems** has highlighted the **type and strength of interactions** that occur between the chemical species present in the complex;
- The ability of polyacrylate-surfactant systems to accommodate various compounds has been demonstrated by solubilizing the pyrene and, **for the first time, the 3-methoxybenzantrone**. The findings could be useful for the solubilization of other hydrophobic compounds in such systems in which **three kinds of hydrophobic microdomains** (i.e., surfactant micelles, intracoil microdomains of the hydrophobic modified polyacrylate, surfactant–polymer complex) are present.

Results dissemination

The results presented in this PhD thesis have been materialized in three papers published in international journals. A great part of the data accumulated over the years of doctoral studies were presented at international and national scientific events, in total four oral and seventeen poster presentations.

List of papers published on the PhD thesis theme:

(1). Formation and hosting properties of polyacrylate–surfactant complexes, L. Aricov, A. Băran, E.L. Simion, I.C. Gîfu, D.F. Anghel, V. Răditoiu, *Colloid and Polymer Science (2017)* DOI:*10.1007/s00396-017-4102-0* (**main author**). Impact Factor – 1,890;

(2). Aqueous solutions of associative poly(acrylates): Bulk and interfacial properties. L. Aricov, H. Petkova, D. Arabadzhieva, A. Iovescu, E. Mileva, K. Khristov, G. Stîngă, C.F. Mihăilescu, D.F. Anghel, R. Todorov. *Colloids and Surfaces A: Physicochemical and Engineering Aspects (2016) 505:138–149* (**main author**). Impact Factor – 2,760;

(3). New insights into the self-assembling of some hydrophobically modified polyacrylates in aqueous solution. L. Aricov, A. Băran, E.L. Simion, I.C. Gîfu, D.F. Anghel, V. Jerca, M. Vuluga, *Colloid and Polymer Science (2016) 294:667–679* (**main author**). Impact Factor – 1,890;

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