



Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 70th anniversary

INFLUENCE OF BORAX AND A HYDROPHOBICALLY MODIFIED SODIUM POLYACRYLATE WITH LOW MOLECULAR WEIGHT ON SDS AGGREGATION

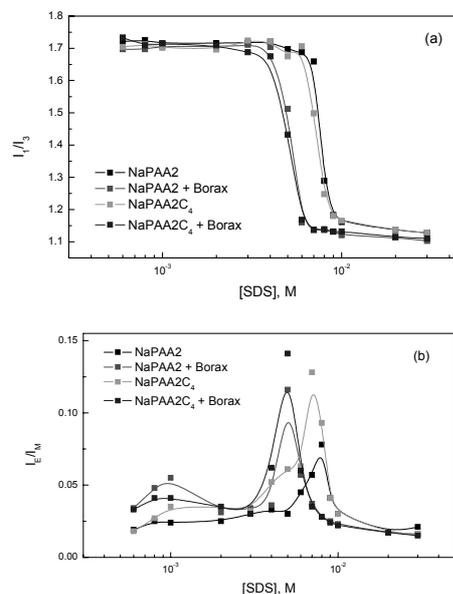
Elena Livia SIMION,^a Gabriela STÎNGĂ,^{a*} Ludmila ARICOV,^a Dumitru Mircea VULUGA^b
and Dan-Florin ANGHEL^{a*}

^a Colloids Chemistry Laboratory, "Ilie Murgulescu" Institute of Physical Chemistry, Roumanian Academy,
202 Spl. Independenței, 660021 Bucharest, Roumania

^b Centre of Organic Chemistry "Costin D. Nenițescu", Roumanian Academy, 202B Spl. Independenței CP 35-108,
060023 Bucharest, Roumania

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A novel hydrophobically modified sodium polyacrylate with low molecular weight (2100 Da, NaPAA2C₄) was obtained by grafting the precursor polymer (NaPAA2) with 2.4 % mol butylamine. The influence of grafted and ungrafted polymers on the micellization of the most common anionic surfactant – sodium dodecyl sulfate (SDS) – was investigated by surface tension, electrical conductivity and steady-state fluorescence. The effect of the borax upon the aggregation process of these polymer-surfactant mixtures was followed. The butyl graft and borax promoted the adsorption of SDS at air/water interface. The mobility of the sodium counterions was affected by the presence of polymer or borax. Although, the butyl graft has a low hydrophobicity, the pyrene as fluorescent probe was able to sense the small hydrophobic change, as evidenced by the polarity index and assessing the excimer formation. The obtained results show that the SDS interacts with hydrophobically modified sodium polyacrylate with short n-alkyl chain. Moreover, the borax affects more efficient the association process between polymer and surfactant.



INTRODUCTION

Since they were first synthesized by Magny,¹ hydrophobically modified poly(acrylic acid)s and polyacrylates have been intensively studied due to their ability to form inter- and intramolecular

aggregates in aqueous solutions.^{2,3} Over the years, their interaction with anionic, cationic and nonionic surfactants has also been investigated.⁴⁻⁶ These polymer-surfactant (PS) mixtures mainly interact by hydrophobic, electrostatic and hydrogen bonding.⁶ Understanding how the interactions take

* Corresponding authors: gstinga@gmail.com and danflorin.angel@gmail.com, Phone: + 40 21 312 1147

place in these systems is important because they are used as viscosity modifiers,⁷ surface coatings,^{8,9} stabilizers for oil drilling fluids,¹⁰ etc.

On the other hand, the PS complexes are responsive to the addition of salt in their solution. Borax is an inorganic electrolyte that has applications in house-hold products, medicines, gold mining, insecticides, etc.¹¹ In a previous work we evaluated the effect of this electrolyte upon the interaction between a fluorescently modified poly(acrylic acid) and sodium dodecyl sulfate (SDS), and compared it with a more common salt such as sodium chloride.¹² Surprisingly, the data indicated that borax was able to decrease the critical aggregation concentration (CAC) of the polymer-surfactant complexes, at high pH. It was demonstrated that the PS associates were stabilized due to transient H-bonding between the carboxyl groups of the polymer and borax, as well as between borax and the sulfate groups of SDS.

The aim of this paper is to investigate the aggregation of hydrophobically modified sodium polyacrylate with a surfactant of same charge like SDS in the absence or presence of borax. For this purpose, a new specimen of sodium polyacrylate with low molecular weight of 2100 Da was grafted with 2.4 % mol butylamine. To the best of our knowledge, the interaction of SDS with hydrophobically modified sodium polyacrylates with low molecular weight and short n-alkyl chain has not been studied yet. The achieved information is important to design new materials responsive to different stimuli (surfactant, inorganic electrolyte) with ability of drug delivery.

EXPERIMENTAL

Materials

The following substances were used for the synthesis of the hydrophobically modified polymer with low molecular weight and short n-alkyl chain: sodium poly(acrylate) with molecular weight of 2100 - NaPAA2 (Fluka), butylamine (99.5%, Sigma-Aldrich), anhydrous N-methyl-2-pyrrolidone (99.5%, Sigma-Aldrich), *N,N'*-dicyclohexylcarbodiimide

(99 %, Sigma-Aldrich), sodium hydroxide (98 %, Lach-Ner), methanol (99 %, Chimopar), and a cation exchange resin from Sigma-Aldrich, DOWEX 50. The resin was employed to transform the polymer in acidic form (HPAA2), because the grafting occurs only between the carboxyl and amine groups. The obtained HPAA2 was recovered from aqueous solution by freeze-drying.

For the physico-chemical determinations the following substances were used: sodium dodecyl sulfate - SDS ($\geq 99\%$, Fluka), di-natriumtetraborate-decahydrate - borax ($\geq 99.5\%$, Merck), pyrene - Py ($\geq 99\%$, Sigma-Aldrich), cyclohexane ($\geq 99.9\%$, Sigma-Aldrich) and ultrapure deionized water prepared with a MilliQ system.

NaPAAC₄ synthesis

The new specimen, the sodium polyacrylate with molecular weight 2100 grafted with 2.4 % mol butylamine, was obtained by adapting a previously described synthesis.² A brief procedure is given below. The amidation of polyacrylic acid was made by reacting the butylamine with the carboxyl group of HPAA2 at 60 °C in the presence of *N,N'*-dicyclohexylcarbodiimide in *N*-methyl-2-pyrrolidone as a solvent. The HPAA2 modified was neutralized and precipitated in NaOH (40 %). The new synthesized polymer was designated by the acronym NaPAA2C₄. The first digit is assigned to the molecular weight of the parent NaPAA2 polymer, while the C₄ corresponds to butylamine. The resulting polymer (See Figure 1) was purified by dialysis through cellulose ester membranes with a molecular weight cut-off of 100-500 Da (Spectrum Laboratories Inc.), and recovered as a white fluffy solid by freeze-drying.

To confirm the functionalization and to calculate the amount of butyl grafted on the polymer's backbone, ¹H-NMR measurement was performed.

FT-NMR spectrum was recorded on a Varian Gemini 2000 (¹H frequency 300MHz) spectrometer, at 50 °C, using a delay of 10 s, 256 fid's/spectrum. The synthesized polymer (NaPAA2C₄) was dissolved in DMSO-D₆. A more detailed procedure signals attribution and grafting degree calculus was previously reported.² Figure 2 presents the ¹H-NMR spectra of NaPAA2C₄. The signal in the region 0.75 ÷ 0.9 ppm accounts for the three protons from C4-methyl in butyl. The complex signal in 1 ÷ 2.4 ppm region accounts for the 2 x 2 protons from C2- and C3-methylenes in butyl and all n x 3 protons of the polymer backbone. The consistency of the sample can be checked comparing the C4-methyl signal of 3 protons with the C1-methylene signal of 2 protons, at about 3.1 ppm, in butyl, if it is not overlapped. Having the methyl signal set at 3 units and all signals scaled accordingly, the grafting degree (%) is obtained with the relation: $G = 100/(N-4)/3$. The result indicated a grafting of 2.4 % mol butylamine.

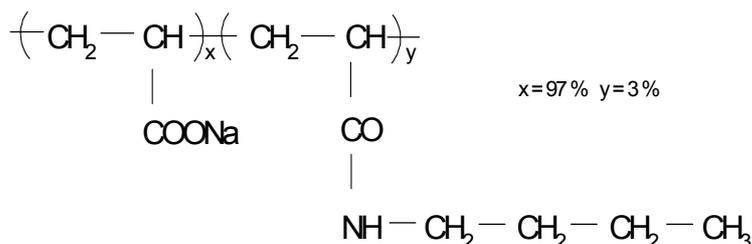


Fig. 1 – The structure of the synthesized NaPAA2C₄ (y = the theoretical grafting degree).

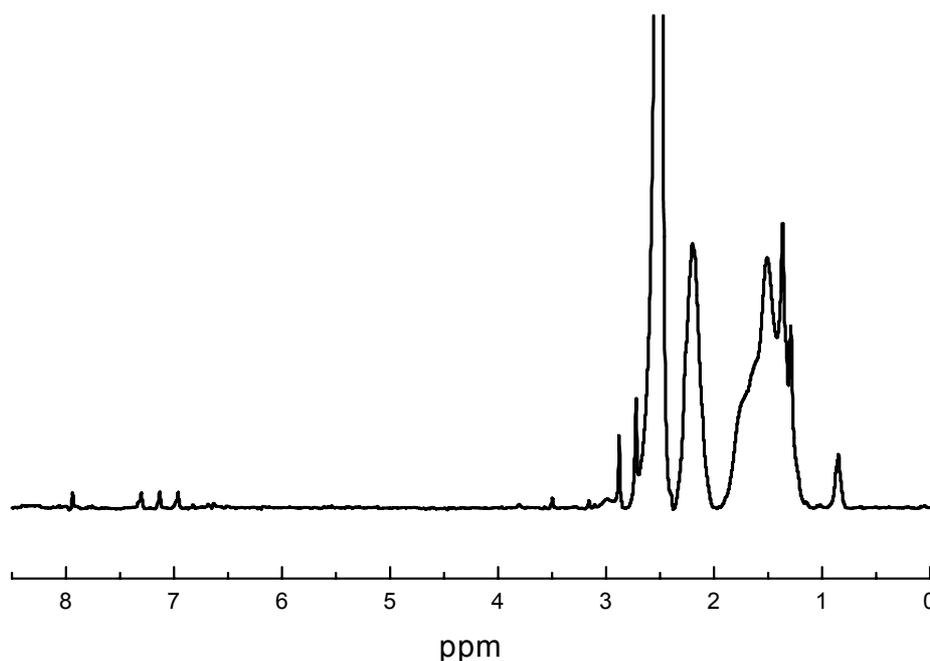


Fig. 2 – ^1H -NMR spectrum of the synthesized polymer.

Methods

Surface tension measurements were carried out with the Du Nouty ring method using a Krüss K11MK3 tensiometer, at room temperature. Electrical conductivity was measured with a pH/ISE Orion 4 Star Benchtop conductometer. All steady-state fluorescence measurements were conducted on a Fluoromax-4 Horiba Jobin Yvon apparatus, using Py as a fluorescent probe. The emission spectra were recorded between 360 and 600 nm with the excitation set at 335 nm. The excitation and emission slits were 2, and respectively, 1 nm.

Sample preparation

The samples used in surface tension and electrical conductivity measurements were prepared by mixing the adequate amounts of stock solutions of polymer (4 g/L), SDS (0.1 M) and borax (0.1 M). The final polymer concentration in all samples was 0.04 g/L, well below the overlapping concentration. The surfactant concentration range varied between 6×10^{-4} M and 3×10^{-2} M SDS, while the final borax concentration was of 5×10^{-3} M. The samples for fluorescence measurements had a final Py concentration of 1×10^{-6} M.

RESULTS AND DISCUSSION

Surface tension

To assess the surface activity of SDS at air/water interface, in the presence of both ungrafted and grafted polymer with butylamine, without and with borax, the surface tension (ST) of aqueous solutions has been measured. Figure 3a shows the ST isotherms of SDS with and without polymers. All the isotherms have a concave region

above 4×10^{-3} M SDS, which is due to the presence of dodecanol – an impurity that was previously found to come from the surfactant's synthesis.⁴ On the one hand, the concave region is more evident for NaPAA2C4-SDS system. On the other hand, the minimum of the concave region was used to determine the critical micelle concentration (CMC) of the surfactant or the critical aggregation concentration (CAC) of the PS mixture. For the surfactant alone, the ST minimum of 35 mN/m allows the detecting of CMC at 7.5×10^{-3} M, a value which is in agreement with the literature data.¹² The solutions containing NaPAA2 had a ST minimum of 33 mN/m at 5×10^{-3} M SDS, while the ones with NaPAA2C₄ exhibit a minimum of 31 mN/m at 6×10^{-3} M SDS. The minimum in ST isotherms marks the beginning of surfactant's micellization on the polymer backbone or CAC. The results in Figure 3a attest that the hydrophobically modified polymer increases the adsorption capacity of SDS at air/water interface.

Figure 3b illustrates the isotherms of the same mixtures with addition of 5×10^{-3} M borax. These systems have lower surface tensions, proving that the salt promotes the adsorption of the surfactant molecules at air/water interface. The phenomenon is due to the screening effect induced by the inorganic electrolyte on the charges of the ionic surfactant.¹² The concave region appears again in the polymer systems, but is less pronounced than for the systems without salt. This means that polymer-surfactant aggregates in the presence of

borax are more capable to solubilizing the alcoholic impurity. All three critical concentrations (CMC and both CAC) for the systems with borax are equal to 4×10^{-3} M SDS. In a previous work we evaluated the surface activity of SDS in the presence of a similar amount of borax and poly(acrylic acid) with molecular weight of 25000 Da grafted with 3 % mol 1-naphthylmethylamine as fluorescent label.¹² The critical concentrations obtained were of 4×10^{-3} M SDS, which is similar to the result of the present study. Therefore, it is important to stress that the molecular weight of the polymer and the kind of grafted chain have little influence on SDS aggregation, whereas the borax has the main role.

Electrical conductivity

The formation of PS complexes and the borax's effect upon the aggregation capacity of SDS was further investigated by electrical conductivity. Figures 4 show the obtained conductivities of SDS

with and without polymers (a) and also with borax (b). In Figure 4a all the breakpoints appear at 8×10^{-3} M SDS, denoting that the polymers do not influence the starting point of micellization for the surfactant. Also, conductivities have lower values for the polymer-surfactant mixtures, indicating that in the presence of polymers the ions' mobility is smaller. Figure 4b shows the evolution of the electrical conductivity of the PS systems with an addition of 5×10^{-3} M borax. As expected the inorganic salt increased the conductivities due to its additional counterions. The breakpoint in the electrical conductivity of the surfactant and borax systems occurs at a lower concentration than for the SDS alone, namely at 5×10^{-3} M SDS. For the NaPAA2-SDS system the aggregation concentration was 6×10^{-3} M SDS, while for the NaPAA2C₄ of 5×10^{-3} M SDS. Similar to the results in previous work,¹² the delimitation between the aggregation of the surfactant on the polymer coil and the saturation of the polymer with SDS was not observed in the systems with borax.

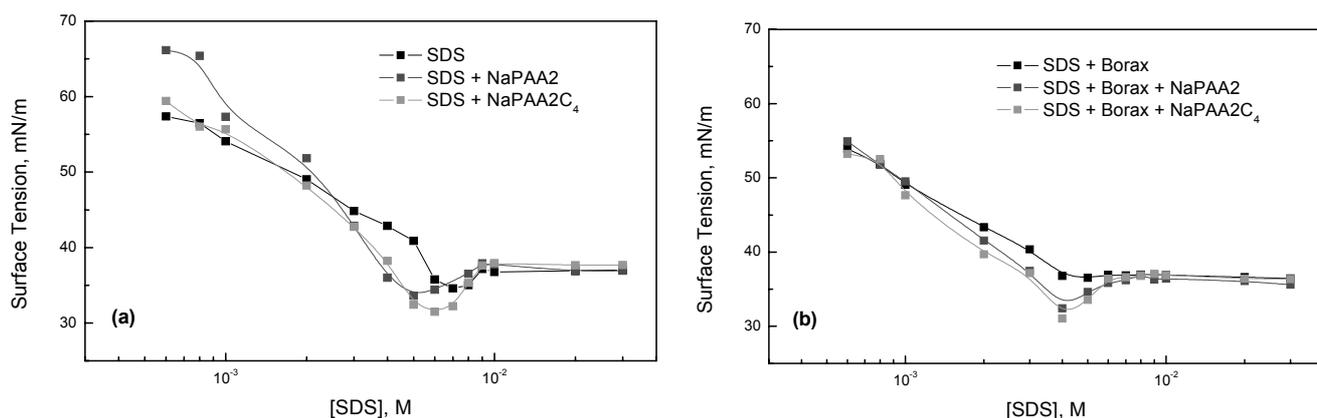


Fig. 3 – ST isotherms of SDS with and without NaPAA2 and NaPAA2C₄ in the absence of salt (a) and in the presence of 5×10^{-3} M borax (b).

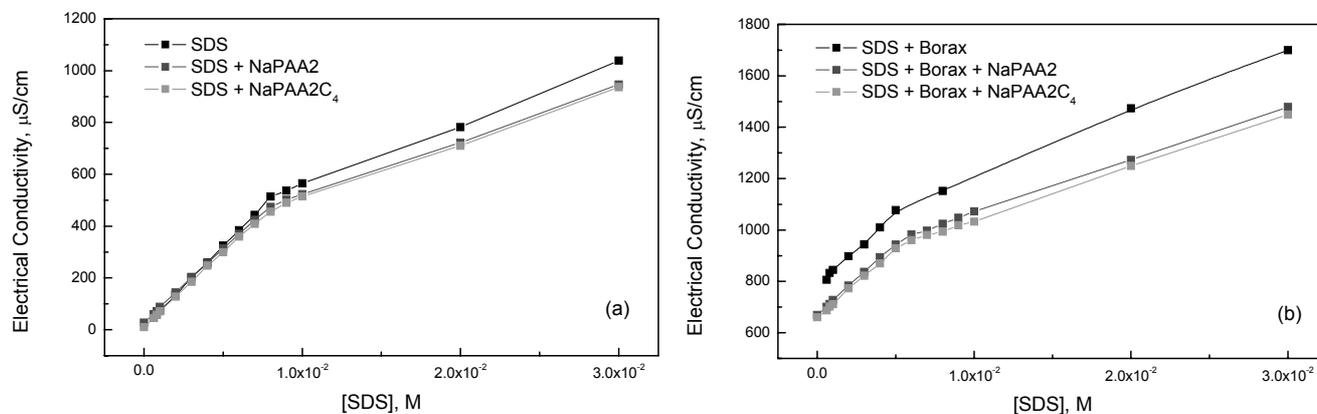


Fig. 4 – Electrical conductivity of SDS without and with NaPAA2 and NaPAA2C₄ (a) and in the presence of 5×10^{-3} M borax (b).

To obtain information about the free sodium counterions, the linear regression method has been used. The micellar ionization degree (α) was calculated as the ratio of slopes above and below the breaking points.¹³ Table 1 illustrates the obtained α values for SDS alone or for the mixture of surfactant with ungrafted or grafted polymer, in the absence or presence of borax.

Table 1

Micellar ionization degrees (α) of the studied systems

| System | α |
|------------------------------------|----------|
| SDS | 0.379 |
| SDS + NaPAA2 | 0.369 |
| SDS + NaPAA2C ₄ | 0.366 |
| SDS + Borax | 0.444 |
| SDS + NaPAA2 + Borax | 0.374 |
| SDS + NaPAA2C ₄ + Borax | 0.370 |

The value of α parameter for SDS alone is in good agreement with that found in literature.¹⁴ The borax increases the micellar ionization degree. It is noteworthy that by adding of salt the degree of ionization increases, the dissociation of surfactant ions is promoted and the screening of charges influences the micellization process of SDS.¹² When adding polymer to the system, α value decreases, because the polymer significantly lowers the mobility of sodium counterions.¹⁵

Steady-state fluorescence

More insight into the studied polymer-surfactant-borax systems has been obtained by means of the steady-state fluorescence measurements. Pyrene (Py) is a polycyclic aromatic hydrocarbon that is frequently used as fluorescent probe, due to its ability to sense the micro-polarity of the environment in which it resides.¹⁶ At concentrations around 10^{-6} M, the emission spectrum of Py monomer has four vibronic peaks (I_1 , I_2 , I_3 and I_5) of high intensities at wavelengths of 371, 377, 382 and 391 nm and a shoulder of lower intensity (I_4) at 387 nm. At higher concentrations, a broad and unstructured emission appears between 430 and 600 nm, with a maximum centered at 470 nm, corresponding to excimer formation, with intensity I_E .¹² The monomer intensity (I_M) was determined from the mean of first and fifth peak intensities. In the following we will use the peak intensities described above to obtain the I_1/I_3 and I_E/I_M ratios.

Figure 5a shows the variation of I_1/I_3 called the polarity index (PI), obtained by changing the

surfactant concentration, in the presence of both polymers and salt. It is well known that in water the PI value is approximately 1.8, while in ethanol and hydrocarbon media, the values are 1.2, and respectively 0.58.¹⁶ In micellar media, Py is located in the palisade layer of the aggregates, due to a higher hydrophobicity than that of water.⁶ Our polarity indexes varied between 1.39 and 1.43, as expected for a micellar environment.¹⁷ The sequence was as follows: $PI_{(NaPAA2C_4+Borax)} < PI_{(NaPAA2+Borax)} < PI_{(NaPAA2C_4)} < PI_{(NaPAA2)}$. The borax systems have lower PI indicating that the salt creates more hydrophobic environments for Py to reside in.^{12,18} As expected, the grafted polymer offers more hydrophobic micro-domains for the probe.⁴ In this study, for all systems with borax, a pH of about 9 was found. The ungrafted and grafted polymers contain many carboxyl groups. At high pH, the carboxylate groups are ionized, and the polymer chain is unfolded. The interaction between a polymer and a surfactant with the same charge should not happen due to the electrostatic repulsions. Nevertheless, the lower value of the PI for systems with borax indicates an interaction which occurs between the sulfate groups of SDS or the carboxyl groups of polymers and borax.¹² Using a Boltzmann function described by Equation (1), we obtained the CAC values of the systems as the middle points of the sigmoid curve.

$$y = A_2 + (A_1 - A_2)/(1 + \exp((x-x_0)/dx)) \quad (1)$$

where y is the I_1/I_3 ratio, A_1 , A_2 and A_3 are the middle, the upper and the lower limits of the sigmoid, x is the SDS concentration and x_0 the width of the sigmoid curve. In Table 2 the obtained CAC values are given.

Table 2

CAC values obtained from steady-state fluorescence measurements

| System | CAC, M |
|------------------------------------|----------------------|
| SDS + NaPAA2 | 8×10^{-3} |
| SDS + NaPAA2C ₄ | 7.5×10^{-3} |
| SDS + NaPAA2 + Borax | 5.5×10^{-3} |
| SDS + NaPAA2C ₄ + Borax | 5×10^{-3} |

The CAC values from steady-state fluorescence are close to the results obtained by surface tension and electrical conductivity. The data confirm that the labeled polymer promotes the surfactant micellization in the absence and presence of salt. However, the SDS concentration at which this process happens is small (about 0.5×10^{-3} M).

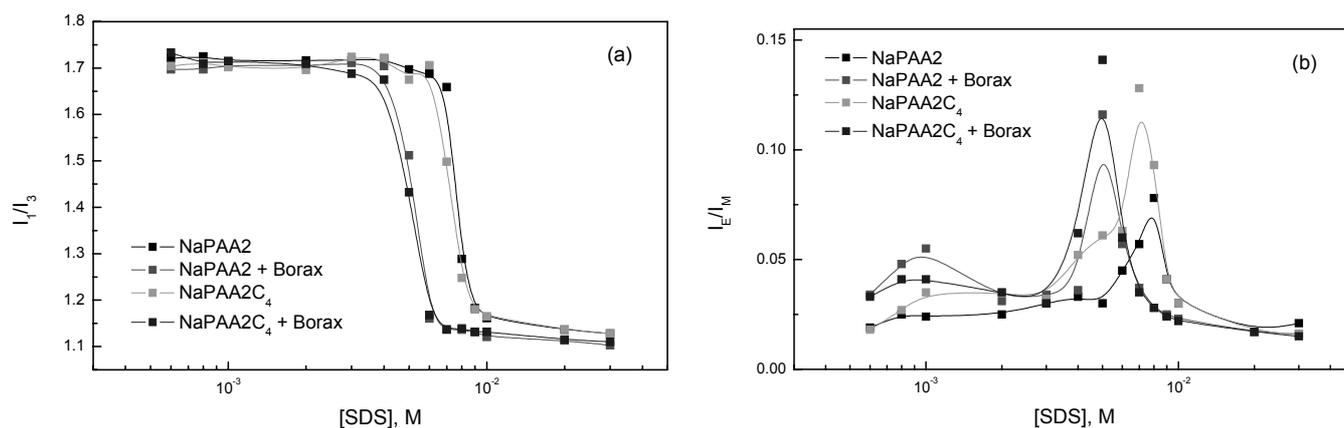


Fig. 5 – PI of pyrene probe vs. SDS concentration in the presence of polymers and 5×10^{-3} M borax (a); I_E/I_M of pyrene probe vs. SDS concentration in the presence of polymers and 5×10^{-3} M borax (b).

Figure 5b shows the I_E/I_M ratios *versus* the surfactant concentration in the presence of both polymers, with and without 5×10^{-3} M borax. The result is an indicator of the ability of Py monomers to form dynamic excimers. At low surfactant concentration the ratios are small. By increasing the SDS concentration, the I_E/I_M ratio begins to grow. At CAC where the I_E/I_M ratio reaches a maximum value, more Py molecules are solubilized in the micelles and the formation of excimer is favored. Above CAC, the I_E/I_M ratio decreases due to pyrene distribution in more polymer-SDS aggregates. The maximum of the I_E/I_M varies as follows: I_E/I_M (NaPAA2) < I_E/I_M (NaPAA2+Borax) < I_E/I_M (NaPAA2C4) < I_E/I_M (NaPAA2C4+Borax), and signifies that excimer formation is favored in a hydrophobic microenvironment of SDS, borax and labeled polymer.

CONCLUSIONS

The association of SDS with unmodified or hydrophobically modified sodium polyacrylates of low molecular weight and short *n*-alkyl chain, in the absence or presence of borax, was investigated by means of surface tension, electrical conductivity and steady-state fluorescence. The results obtained revealed that the hydrophobically modified polyacrylate enhances the adsorption of SDS at the air/water interface, inhibits the dissociation of surfactant ions and creates more hydrophobic microenvironment with surfactant molecules in comparison with its parent. The electrostatic and hydrophobic interactions acted mutually in our PS systems without and with borax. However, the

H-bondings between the sulfate groups of surfactant or the carboxyls of polymer and borax entail the formation of more hydrophobic PS complexes than those without borax.

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