



## PROBING THE MICELLE/WATER INTERFACE BY NON-RADIATIVE ENERGY TRANSFER

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The non-radiative energy transfer (NRET) between the pyrene labeled poly(acrylic acid) (PAA-Py) dissolved in bulk solution and naphthalene (Np) solubilized in surfactant micelles is studied at various pH values and salt concentrations. Additional information was obtained from DLS measurements. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT), sodium dodecyl sulfate (SDS) and decaethylene glycol mono-tetradecyl ether (C<sub>14</sub>EO<sub>10</sub>) are the surfactants considered. NRET is estimated as the ratio between the emission intensity of pyrene and that of naphthalene ( $I_{Py}/I_{Np}$ ) and depends on surfactant, pH, and salt concentration. For SDS,  $I_{Py}/I_{Np}$  is not affected by changing the pH from 2 to 11. AOT shows an initial decrease of  $I_{Py}/I_{Np}$  ratio with increasing pH followed by a leveling off above a pH value exceeding the  $pK_a$  of PAA-Py. The nonionic surfactant has a peculiar behavior with a minimum of  $I_{Py}/I_{Np}$  around the  $pK_a$  of PAA-Py and a plateau at pH 7. A maximum of NRET appears in the SDS micellar system at a NaCl concentration equal to 0.01 M. These behaviors are explained taking into account the obtained values of Förster radius, the distance between acceptor and donor, the quantum yield of donor and the efficiency of energy transfer.

### INTRODUCTION

A matter of major interest for scientists working on polymer-surfactant systems is the driving force behind the interaction. In mixtures of oppositely charged surfactants and polymers, a decisive role is played by the electrostatic attraction.<sup>1,2</sup> When the solution contains a nonionic surfactant and a polyelectrolyte, the interaction involves hydrophobic attraction between the species.<sup>3,4</sup> If the surfactant and polyelectrolyte have the same charge, the electrostatic repulsion hinders the formation of intermolecular aggregates.<sup>5</sup> Non-radiative energy transfer (NRET) is a powerful tool to investigate the phenomena appearing at nanometric level in polymer, surfactant, polymer-surfactant mixtures, and in life sciences. NRET is able to shed light on the interpenetration of polymer chains,<sup>6</sup> and on the interactions between proteins,<sup>7,8</sup> proteins and biomaterials,<sup>9,10</sup> and proteins and drugs.<sup>11,12</sup> It is also used in bioanalysis,<sup>13</sup> and to monitor the distribution of proteins and lipids in membranes.<sup>14</sup> The method

describes the transfer of energy between an excited donor and a ground-state acceptor through non-radiative dipole-dipole coupling. NRET depends on the distance between donor and acceptor, the spectral overlap of donor emission spectrum and acceptor excitation spectrum, and the relative orientation of the dipole moments of donor and acceptor. Naphthalene (Np) and pyrene (Py) with a "Förster radius" of about 29 Å,<sup>15,16</sup> are often used as donor-acceptor pair in NRET experiments.<sup>17,18</sup> Previously we used this technique to study the conformational changes and interactions between poly(acrylic acid) separately labeled with naphthalene and pyrene.<sup>19</sup>

In this paper we use NRET as a means to probe the micelle-water interface. Toward this end, we confined the Np donor in surfactant micelle and dissolved the pyrene-labeled poly(acrylic acid) (PAA-Py) acceptor in bulk solution. The obtained results show that NRET depends on surfactant, pH and ionic strength. Additional information is obtained by dynamic light scattering (DLS).

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## EXPERIMENTAL

### Materials

Naphthalene, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and sodium dodecyl sulfate (SDS) were reagent grade chemicals purchased from Fluka-Sigma-Aldrich, Bucharest, Roumania and used as received. Decaethylene glycol monotetradecyl ether (C<sub>14</sub>EO<sub>10</sub>) was a product of Nikko Chemicals, Tokyo, Japan and used without further purification. Sodium chloride was obtained from Chimopar S.A. Bucharest, Roumania and used as received. PAA-Py with  $M_n = 150,000 \text{ gmol}^{-1}$  was synthesized and characterized as previously reported.<sup>17</sup> It has on average 1 pyrene group per 32 acrylic acid monomer units. The structure of polymer is presented in Scheme 1. Milli-Q water with a resistivity of 18 MΩcm was used to prepare solutions. For NRET experiments, the concentration of anionic surfactant was chosen to be equal or greater than its critical micellar concentration (CMC) ( $8 \times 10^{-3} \text{ M}$  for SDS and  $3 \times 10^{-3} \text{ M}$  for AOT).<sup>20,21</sup> The nonionic surfactant concentration was greater than its CMC ( $1.8 \times 10^{-5} \text{ M}$ ).<sup>22</sup> Aqueous solutions of 0.1 M NaOH and 0.1 M HCl were used to adjust the pH. Solutions for NRET were prepared at a molar ratio  $[\text{Np}]/[\text{Py}] = 5$ .

### Apparatus

The pH was monitored with an ORION pH-meter, model 420 A, calibrated with standard buffers. The hydrodynamic diameter of the micelle was determined by DLS measurements on a ZetaSizer, Nano ZS, Malvern Instruments. The analysis was performed at a laser wavelength of 633 nm and an angle of 173°, making 10 determinations for each sample. The absorption spectra were recorded on a Varian Cary 100 Bio spectrophotometer. In all experiments the absorbance of the solution at the excitation wavelength was kept below 0.1 to minimize the inner-filter effect and to prevent re-absorption by the acceptor. Fluorescence measurements were carried out on a FLS 920 Edinburgh Instruments. For NRET measurements the excitation wavelength was set at 290 nm, and the emission was recorded between 310 and 550 nm. The excitation and emission slits were set at 3 and 1 nm, respectively. In all the measurements the temperature was kept constant at  $25 \pm 0.1^\circ\text{C}$ .

### Methods

The efficiency of energy transfer,  $E$ , was calculated from measurements of donor intensity at 319 nm, in the absence and presence of acceptor, according to equation (1):

$$E = \left(1 - \frac{I_{DA}}{I_D}\right) \times 100 \quad (1)$$

where,  $I_D$  and  $I_{DA}$  represent the fluorescence intensity of donor in the absence and respectively in presence of acceptor.

According to Förster theory, the NRET efficiency ( $E$ ) is directly related to the distance ( $r$ ) between the donor and acceptor by equation (2):

$$E = \left(1 + \frac{r^6}{R_0^6}\right)^{-1} \quad (2)$$

$R_0$  is the Förster critical distance, at which 50 % of the excitation energy is transferred to the acceptor, and is calculated with equation (3):<sup>23</sup>

$$R_0 = 9.78 \times 10^3 \left(k^2 n^{-4} \Phi_D J(\lambda)\right)^{\frac{1}{6}} \text{ (in } \text{Å)} \quad (3)$$

where,  $k^2$  is a dimensionless parameter that depends on the relative orientation of the donor and acceptor transition moments, that typically is 2/3,  $n$  is the refractive index of the medium,  $\Phi_D$  is the quantum yield of the donor in the absence of the acceptor,  $J(\lambda)$  is the overlap integral, which expresses the degree of spectral overlap between the donor emission and the acceptor absorption (in units of  $\text{M}^{-1}\text{cm}^3$ ) and is given by equation (4):

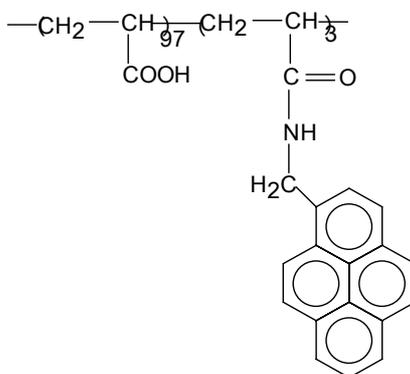
$$J(\lambda) = \frac{\int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda} \quad (4)$$

where,  $F_D(\lambda)$  is the variation of the donor fluorescence intensity with the wavelength  $\lambda$  and is dimensionless,  $\varepsilon_A(\lambda)$  is the variation of the molar absorption coefficient of the acceptor with the wavelength  $\lambda$ , and its units are  $\text{M}^{-1}\text{cm}^{-1}$ .

Fluorescence quantum yields ( $\Phi_D$ ) of the donor in different micellar media were determined by comparison with a reference solution. For this purpose, the following relation was applied to calculate quantum yield:<sup>24</sup>

$$\Phi_D = \Phi_S \frac{A_S F_D n_D^2}{A_D F_S n_S^2} \quad (5)$$

where, the subscripts D and S refer to donor and standard,  $F$  is the integral area of the corrected emission spectrum, and  $n$  the refractive index. The reference used in this study is naphthalene in ethanol, which has a fluorescence quantum yield of 0.21.<sup>25</sup>



Scheme 1 – The molecular structure of PAA-Py.

## RESULTS AND DISCUSSION

### DLS measurements

We monitored by DLS the changes produced by salt and polymer on the size of SDS micelles in aqueous solution. Table 1 illustrates the values of hydrodynamic diameter ( $d_h$ ), pH, refractive index ( $n$ ) and polydispersity index (PDI) of the investigated systems. The polydispersity index is a parameter that reflects the quality of the obtained DLS results. For monodisperse samples, the threshold PDI value is of 0.08, and the 0.08-0.7 range is accepted for polydisperse samples. The PDI data in Table 1 show that all the investigated samples fall in the second category and the reported hydrodynamic diameters are only for guidance.

The results in Table 1 show that the increase of NaCl concentration brings about the growth of the micelle hydrodynamic diameter. The effect can be explained by the decrease of repulsive interactions between the head groups of the surfactant monomers. Adding the salt, the head groups are dehydrated, leading to the increase of the micelle size and the aggregation number.<sup>26,27</sup> In the presence of PAA-Py, it is observed a leveling of the micelle size, irrespective of the amount of added salt. For example, the hydrodynamic diameter equals 3.90 nm at  $10^{-2}$  M NaCl, and 3.91 nm at  $10^{-1}$  M NaCl. This result is somehow intriguing and further work is necessary to explain it.

### NRET Measurements

The results discussed in the following sections are about the influence of pH and salt on NRET between the naphthalene confined in surfactant micelles and PAA-Py dissolved in water.

#### 1. Effect of pH

Fig. 1 shows the emission spectra recorded between 310 and 550 nm at three different pH values by exciting Np confined into the AOT micelles. All spectra show an emission from 310 to 360 nm due to locally excited Np (intensity,  $I_{Np}$ ) with the (0,0) band located at 319 nm. It is followed by pyrene (Py) emission (intensity,  $I_{Py}$ ), which appears beyond 360 nm and is strongly

dependent on pH. At low pH values, Py shows both monomer emission from 360 to 430 nm (intensity,  $I_M$ ) with the (0,0) band located at 378 nm, and excimer emission from 430 to 550 nm (intensity,  $I_E$ ). Py excimer emission is not structured and is centered at about 480 nm. Py emission appears by energy transfer from the Np excited at 290 nm and decreases steeply by raising the pH. In another experiment, the mixed system of pH 2.25 was excited at 346 nm. Excitation at this wavelength produced emission from directly excited Py, with no contribution from naphthalene, since only Py absorbs light of this wavelength. This experiment proves that Py emission originates by energy transfer from Np.

By comparing the emission spectra of the polymer solutions at different pH values, we observed a significant decrease of the Py emission upon the increase of pH. NRET mainly occurs at low pH values, indicating that the distance between the donor and acceptor is appropriate for this phenomenon. At pH = 9.63 the energy transfer is very low and one may safely assume that the distance between the chromophores is longer than twice the Förster radius.<sup>23</sup>

NRET measurements were also done in SDS and  $C_{14}EO_{10}$  micellar systems. The results unveil emission contributions from both Np and Py (spectra not shown). We took as a qualitative measure of the relative extent of the energy transfer the ratio of the emission intensities at 395 nm of Py ( $I_{Py}$ ), to those of the average at 320 nm and 334 nm of Np ( $I_{Np}$ ). On this scale, a greater  $I_{Py}/I_{Np}$  value reflects a higher NRET efficiency. Fig. 2 illustrates the effect of pH on the NRET in AOT, SDS and  $C_{14}EO_{10}$  micellar systems. For SDS and AOT systems, a drop of  $I_{Py}/I_{Np}$  is observed by increasing pH. It is very small, of about 0.5  $I_{Py}/I_{Np}$  units for SDS and of about 3.5  $I_{Py}/I_{Np}$  units for AOT. In both cases, the  $I_{Py}/I_{Np}$  drop is followed by a leveling-off zone situated at pH values of 2.5 for SDS and of 5.8 for AOT. The latter value agrees very well with the  $pK_a$  of PAA-Py, which is 5.7.<sup>17</sup> The plateau appearing in Fig. 2 can be explained by the fact that the increase of pH entails transformation of carboxyl to carboxylate groups. As the pH raises, the PAA acquires more negative charges and adopts an open conformation. This open conformation bears many negative charges that repel the anionic micelles and NRET decreases.

Table 1

Hydrodynamic diameter ( $d_h$ ) of SDS micelles in the absence and presence of salt and PAA-Py, together with pH and refractive index (n) of solutions

[SDS], M	[NaCl], M	[PAA-Py], M	pH	n	$d_h^* \pm \sigma$ , nm	PDI
$8 \times 10^{-3}$	$10^{-2}$	-	5.59	1.333	$3.94 \pm 0.07$	0.342
	$10^{-1}$	-	5.43	1.334	$4.51 \pm 0.07$	0.365
	$10^{-2}$	$0.75 \times 10^{-4}$	5.43	1.334	$3.90 \pm 0.28$	0.600
	$10^{-1}$	$0.75 \times 10^{-4}$	4.78	1.334	$3.91 \pm 0.22$	0.455

\* The values represent the mean hydrodynamic diameter,  $d_h$ , and the standard deviation,  $\sigma$ .

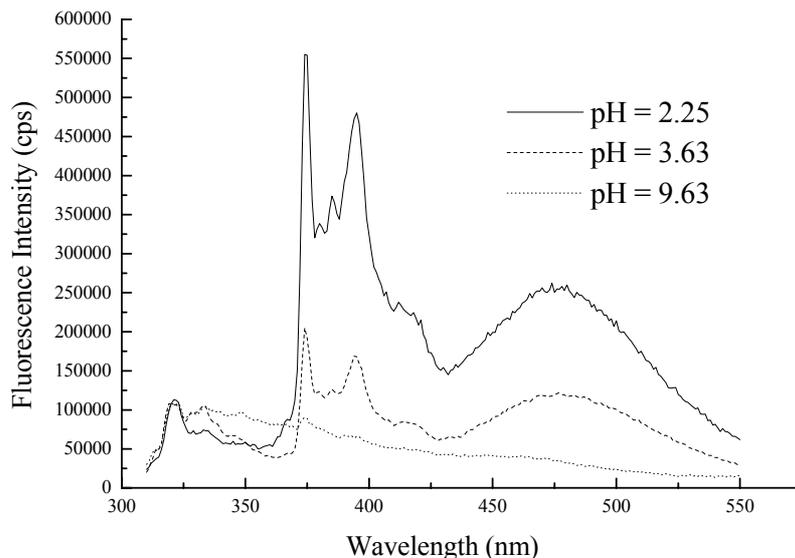


Fig. 1 – Nonradiative energy transfer between Np and PAA-Py in micellar AOT systems, at different pHs. The spectra are normalized with respect to the naphthalene emission.  $[AOT] = 8 \times 10^{-3}$  M.  $[PAA-Py] = 3.27 \times 10^{-6}$  M.  $[Np] = 1.6 \times 10^{-5}$  M.  $\lambda_{ex} = 290$  nm.

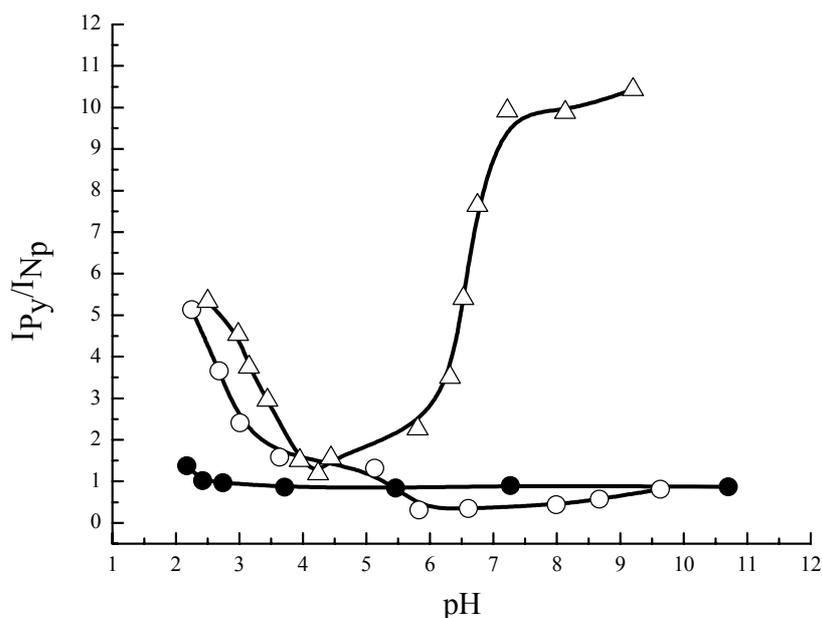


Fig. 2 – The effect of pH on the  $I_{Py}/I_{Np}$  ratio for different surfactant – PAA-Py systems: (○) AOT ( $C_{AOT} = 8 \times 10^{-3}$  M), (●) SDS ( $C_{SDS} = 1.76 \times 10^{-2}$  M), (Δ)  $C_{14}EO_{10}$  ( $C_{C_{14}EO_{10}} = 6 \times 10^{-5}$  M),  $\lambda_{ex} = 290$  nm.

Fig. 2 also shows the change of  $I_{Py}/I_{Np}$  versus pH for  $C_{14}EO_{10}$ . Initially,  $I_{Py}/I_{Np}$  decreases steeply as for AOT. It reaches a minimum value at pH 4.24, then increases and has a plateau above pH 7. The increase of NRET above pH 4.24 can be explained taking into consideration the non-cooperative and cooperative binding of the surfactant molecules onto the polymer.<sup>4</sup> They produce polymer uncoiling, and drives out the Py labels in water. If Py encounters a surfactant micelle containing excited  $Np$ , the donor will transfer energy to the acceptor and the  $I_{Py}/I_{Np}$  will increase. The increase is steeper as the pH increases because the PAA-Py random coil unwinds as it acquires negative charges. However, at pH 7, this phenomenon ceases as revealed by measurements of coil index.<sup>17,28</sup> Therefore, the number of Py labels available for energy transfer becomes constant and explains the plateau of  $I_{Py}/I_{Np}$  above pH 7.

To calculate the distance between donor and acceptor at micellar interface we applied the Förster theory and the values obtained are given in Table 2. They show that the average distance between donor and acceptor is within the 25.0 – 32.9 Å range and obeys the relation  $0.5R_0 < r < 2R_0$ . The obtained value indicates that the energy transfer between the two chromophores occurs with high probability in the studied systems. For the anionic surfactants  $r$  varies in the order: AOT > SDS. The largest distance for AOT may be due to the bulky hydrophobic group that hinders the polymer interaction with the micelle of this surfactant. In the systems with nonionic surfactant, the smallest value of the distance between donor and acceptor is at pH 7.22. At this pH, the PAA coil unfolds and exposes the pyrene labels to water, allowing them to interact with the surfactant micelles containing the solubilized  $Np$  probe. Other parameters characteristic to the energy

transfer like  $J(\lambda)$ ,  $R_0$ ,  $E$ , and  $\Phi_D$  are also given in Table 2. In all the studied micellar systems,  $J(\lambda)$  has values of the same order of magnitude. The anionic surfactants have almost equal overlapping integrals, but smaller than for the nonionic surfactant. For  $C_{10}EO_{14}$ , the  $J(\lambda)$  depends on pH, the highest value being recorded at low pH. For anionic surfactants, SDS has a higher  $E$  than AOT, which is in turn smaller than for  $C_{10}EO_{14}$ . Moreover, the  $E$  of nonionic surfactant depends on pH and increases when pH changes from acidic to neutral. The  $\Phi_D$  values of the donor are quite similar, and do not exceed the value of the  $Np$  standard used to compute them. The highest  $\Phi_D$  is obtained in AOT micelles, and it is in conformity with the branched structure of this surfactant that entails a more loosened packing of the hydrophobic tails into its micelles than in those of SDS that have a linear alkyl chain. This allows to the solubilized  $Np$  to come in the vicinity of micelle surface and to interact easier with the Py label.

## 2. Influence of ionic strength

Fig. 3 presents the effect of sodium chloride on NRET between the  $Np$  confined in SDS micelles and Py grafted onto PAA and dissolved in bulk solution. The data are obtained at pH 5. At salt levels below  $7 \times 10^{-3}$  M, the energy transfer is almost constant describing a plateau. The  $I_{Py}/I_{Np}$  has a mean value of about 0.92, which is very close to that reported in Fig. 2. By increasing the NaCl concentration, the energy transfer increases to a peak value of 2.33 at  $1 \times 10^{-2}$  M NaCl. Then,  $I_{Py}/I_{Np}$  decreases and levels off at a NaCl concentration of  $4 \times 10^{-2}$  M. This behavior can be rationalized taking into account that the inorganic electrolyte affects both the micelles and the polymer.

Table 2

The spectral overlap integral ( $J(\lambda)$ ), the critical transfer radius ( $R_0$ ), the efficiency of energy transfer ( $E$ ), the distance between donor and acceptor ( $r$ ), and the donor quantum yield ( $\Phi_D$ ) in various surfactant systems ( $[Np] = 1.2 \times 10^{-5}$  M;  $[PAA-Py] = 0.75 \times 10^{-4}$  M)

Surfactant and its concentration	$J(\lambda)$ , $M^{-1}cm^3$	$R_0$ , Å	$E$ , %	$r$ , Å	$\Phi_D$
$8 \times 10^{-3}$ M SDS	$1.74 \times 10^{-14}$	24.9	33	28.1	0.11
$8 \times 10^{-3}$ M AOT	$1.57 \times 10^{-14}$	26.8	23	32.9	0.19
$6 \times 10^{-5}$ M $C_{14}EO_{10}$ , pH = 2.98	$3.22 \times 10^{-14}$	28.0	43	29.4	0.12
$6 \times 10^{-5}$ M $C_{14}EO_{10}$ , pH = 4.13	$1.92 \times 10^{-14}$	26.6	43	28.1	0.15
$6 \times 10^{-5}$ M $C_{14}EO_{10}$ , pH = 7.22	$2.22 \times 10^{-14}$	26.6	59	25.0	0.13

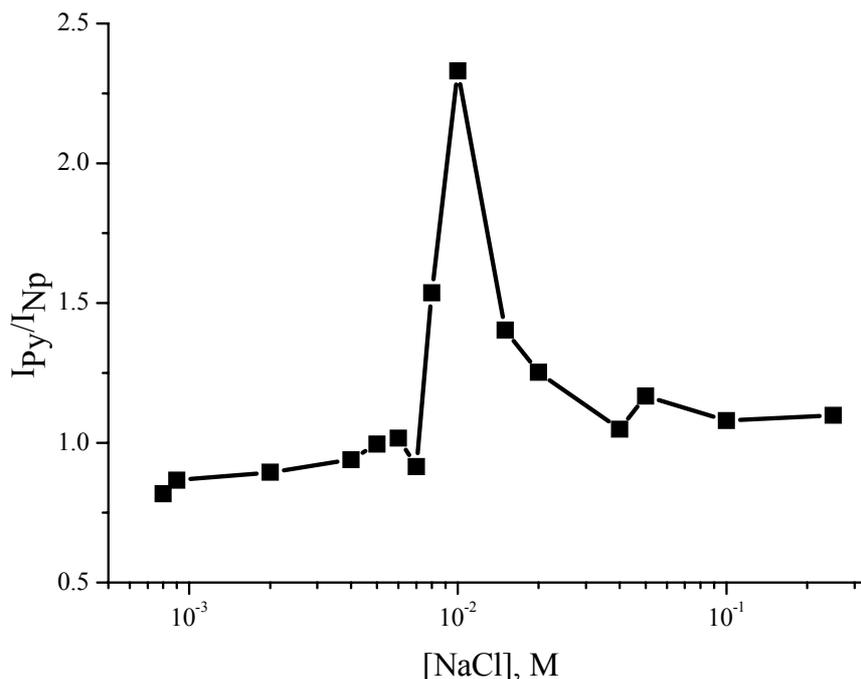


Fig. 3 – The NaCl influence upon the  $I_{Py}/I_{Np}$  in SDS – PAA-Py system. [SDS] =  $8 \times 10^{-3}$  M.

Addition of electrolyte to ionic surfactant solutions decreases CMC and increases the micelle size. For example, the CMC of SDS is  $7.78 \times 10^{-3}$  M (without NaCl) and  $1.72 \times 10^{-3}$  M (in presence of 0.1 M NaCl).<sup>29</sup> The same surfactant has an aggregation number of 60 in water and of about 100 in 0.22 M NaCl aqueous solution.<sup>30</sup> The effect is due to the reduction of the repulsion between the charged head groups of SDS in the micelle, which promotes aggregation.

At the same time, addition of inorganic electrolyte to an aqueous polymer solution induces chain contraction or expansion, as well as conformational or phase transitions. The response depends on polymer structure, its concentration and molecular mass, and on the nature of added electrolyte. For example, neutralization of poly(acrylic acid) by addition of base ionizes the carboxylic groups, expands the macromolecular backbone and transforms the PAA in polyelectrolyte. Addition of sodium chloride to neutralized PAA solution screens the charges and shrinks the polyelectrolyte that adopts a smaller, more entropically favored conformation.<sup>31</sup> In the case of PAA-Py, addition of NaCl screens the polymer charges and enhances the hydrophobic interactions between the pyrene labels. This statement is sustained by our DLS data obtained on PAA-Py at pH 5. Without NaCl, the PAA-Py has a random coil of 55 nm, which decreases to 13 nm in presence of  $10^{-2}$  M NaCl. Taking into account

these results and the fact that  $I_{Py}/I_{Np}$  is only a qualitative parameter that describes NRET we have to stress that the data shown in Fig. 3 are quite complex and require supplementary investigation to fully understand them. However, we have evidence that the distance between donor and acceptor and the efficiency of energy transfer strongly depend on NaCl concentration. For example, at  $10^{-2}$  M NaCl, the distance between Np and Py is the smallest and the efficiency of energy transfer is the highest in the studied systems.

## CONCLUSIONS

The results obtained demonstrate that NRET is an effective technique to acquire information on the molecular interaction between the naphthalene probe solubilized in surfactant micelles and the pyrene label grafted on poly(acrylic acid) and dissolved in bulk solution. The data reveal that NRET depends on surfactant, pH and salt. For SDS, which is a single-chain anionic surfactant, NRET is practically unaffected by pH. For the double-chain AOT, NRET decreases and levels off around the  $pK_a$  of PAA-Py. The nonionic surfactant has a minimum of NRET at  $pK_a$  and a plateau above pH 7. The phenomenon is traced to complex formation between the surfactant and polymer through hydrophobic interaction and multiple hydrogen bondings. The increase of pH

decreases the NRET. At constant pH, a peak value of NRET appears at a NaCl concentration of about  $10^{-2}$  M. The phenomenon is quite complex and investigations by time-resolved fluorescence and other techniques are now in progress to clarify it.

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