On the Statistical Physics Modeling of Dye Adsorption onto Anionized Nylon: Consequent New Interpretations

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ABSTRACT: Experimental adsorption isotherm of two basic dyes: Basic Blue 3 and Basic Red 24 from aqueous solution onto modified nylon 6,6 were analyzed by using a double layer adsorption model with two energy levels. Such model is based on statistical physics treatment. The parameters involved in the analytical expression of this model such as the fraction or the number of adsorbed dye molecule(s) per site, n, the receptor sites density, N_M, and the energetic parameters, c_1 and c_2, were determined by fitting the experimental adsorption isotherms at four temperatures between 293 and 353 K with different degrees of grafting between 20 and 80%. The evolution of these parameters versus temperature and the grafting percent allows us to interpret and better understand this adsorption process at molecular level. Two different behaviors of the two dye molecules were highlighted according to their localized and non localized charges. The configurational entropy at various temperatures has also been studied. This parameter allowed to deduce some results related to the evolution of the disorder at the adsorption surface. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1091–1102, 2012

Key words: adsorption; basic dyes; modeling; statistical physics; grand canonical ensemble

INTRODUCTION

The presence of dyes in wastewater derived from different industries has several harmful effects on the environment.[1–5] For this reason, several methods[6–9] have been used to limit the effects of these dyes such as the adsorption. It reveals efficient solution to treat a large quantity of wastewater.

To understand and interpret the adsorption process, many authors have established different empirical adsorption isotherm models.[10–13] Thus, the interest to investigate such phenomenon in an experimental way as well as a theoretical method is arise.

In this study, an attempt is made to give new physical interpretations of such adsorption process at microscopic levels by using a statistical physics model that can describe the adsorption isotherms. The development of the model, based on the grand canonical partition function, provides an explanation of the dye molecules behavior during the adsorption process. The experimental adsorption isotherms of two basic dyes (BB3 and BR24) onto modified nylon were fitted with different models and a double layer model with two energy levels has been selected for the interpretation. This adequate model shows four parameters such as n, N_M, c_1, and c_2 which can describe the adsorption process.

MATERIALS

The support used for the immobilization of pollutant basic dyes is the methacrylic acid-grafted nylon (MAA-nylon) which was obtained by treating nylon-6,6 fibers with methacrylic acid (MAA). Four degrees of grafting (%G) were used, 20, 40, 60, and 80%. The experimental details have been reported elsewhere in our previous work.[14]

The two basic dyes used in the experiments were Basic Blue 3 (BB3) and Basic Red 24 (BR24). Both were used in their commercially available form blended with mineral salts to adjust their dyeing power. The chemical structures of these dyes are depicted in Figure 1. The first dye, BB3, possesses a delocalized positive charge (due to resonance phenomena) in aqueous solution but the second one, BR24, possesses a positive localized charge on the quaternary ammonium group. The two dyes were supplied by Bayer with a purity of 85%. The dyes, BB3 and BR24, have molecular weight of 492 and 360 g/mol, respectively. Although the experimental study has been described with details in our previous publication,[14] in the present manuscript, it is just recall the experimental conditions related to the adsorption of
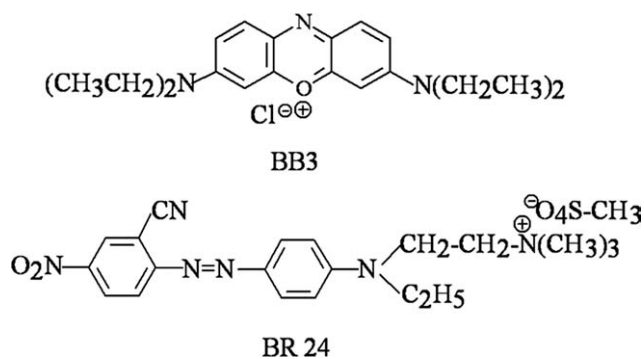
Figure 1 Chemical structure of two basic dyes BB3 and BR24.

two dyes BB3 and BR24 on the MAA-nylon. As it was described in our previous work,[14] the affinity of MAA-nylon anion exchanger for the adsorption of basic dyes was determined by stirring 0.1 g of prepared material and 100 mL of an aqueous solution with a given initial dye concentration mechanically in an Ahiba Nuance® laboratory machine (Salvis AG, Reussbühl, Switzerland) for 2 h at a given temperature (20, 40, 60, and 80°C). The equilibrium concentration (c) of the remaining dye was determined using an Uvikon 941 Plus® spectrophotometer (Kontron Instruments, Milan, Italy) at the maximum absorbance wavelength ($\lambda_{BB3} = 654$ nm; $\lambda_{BR24} = 668$ nm). Adsorption isotherms, Q_a versus c, were determined varying two parameters, that is, the %G value of the MAA-nylon material and the temperature of dye solution. Solution pH affects both aqueous chemistry and surface binding sites of the adsorbents which are negatively charged due to the presence of carboxylic groups. Depending on pH, these groups may change their charge. The adsorption of cationic dye solutions (BB3 and BR24) was strongly affected by pH, where the optimum pH for the removal of BB3 and BR24 is between pH 7–8.

METHODOLOGY

The experimental isotherms of the two dyes onto modified nylon were presented in form of adsorbed quantity versus concentration, at equilibrium. These isotherms show that the adsorption quantity increases with concentration to reach a saturation level (Fig. 2). The experimental data were fitted using different theoretical models that we have published elsewhere.[15–18] The Langmuir model was also tested since it was used by many authors to evaluate the adsorbed quantity. The fitting criterion in the present investigation is the well known correlation coefficient R^2. The ideal fitting is obtained when the value of R^2 is close to the unit. The values of R^2 obtained from various models are not much spread. However, the interpretation is based on the results given by the double layer model

with two energy levels. The choice of such model is reinforced by the two reasons of electric neutrality and chemical potential equilibrium.

It can be noticed that the double layer adsorption model with two energy levels is in a good agreement with the experimental isotherms in case of the two dyes BB3 and BR24 (Figs. 3 and 4). Furthermore, two reasons confirm the choice of this model. The first is an electric neutrality reason. Indeed, the adsorbent surface is negatively charged while the solution contains the dye molecules which are positively charged. So, an electrostatic attraction occurs and the dye molecules are adsorbed onto the surface in the first layer. The second is to equilibrate the chemical potential. Indeed, the solution is still more concentrated although the first layer is adsorbed and more layers can be adsorbed. From the second layer, an electrostatic repulsion occurs which decreases the adsorbed quantity at the following layers. Consequently, the number of adsorbed layers will be limited. However, we are based on our interpretation on the results given by the double layer model with two energy levels. The choice of such model is reinforced by the two reasons of electric neutrality and chemical potential equilibrium as explained previously. Furthermore, it will be easy to interpret the microscopic process with a double layer model in our case. Two different energy levels will be attributed, respectively, to the two adsorbed layers since the first is directly in contact with the adsorbent surface and the second is about an adsorbate-adsorbate interaction.

The double layer adsorption model with two energy levels is established using a statistical physics treatment. Indeed, to treat such adsorption problem with a statistical physics, we make some assumptions.[16–18] For this model, we assume that the first adsorbed layer has an adsorption energy level ε_1 and the second one has a different adsorption energy level ε_2 which should be lower than the first since the first molecules are adsorbed directly onto the surface and so they have a higher energy.

The grand canonical partition function for one receptor site in such situation is:

$$z_{gc} = 1 + e^{\beta(\varepsilon_1 + \mu)} + e^{\beta(\varepsilon_1 + \varepsilon_2 + 2\mu)} \tag{1}$$

and for N_M identical receptor sites, the total grand canonical partition function is:

$$Z_{gc} = \left(z_{gc}\right)^{N_M}$$

The occupation number for N_M identical receptor sites is therefore given as follow:

$$N_0 = \frac{1}{\beta} \frac{\partial Ln \left(z_{gc}\right)^{N_M}}{\partial \mu} \tag{2}$$
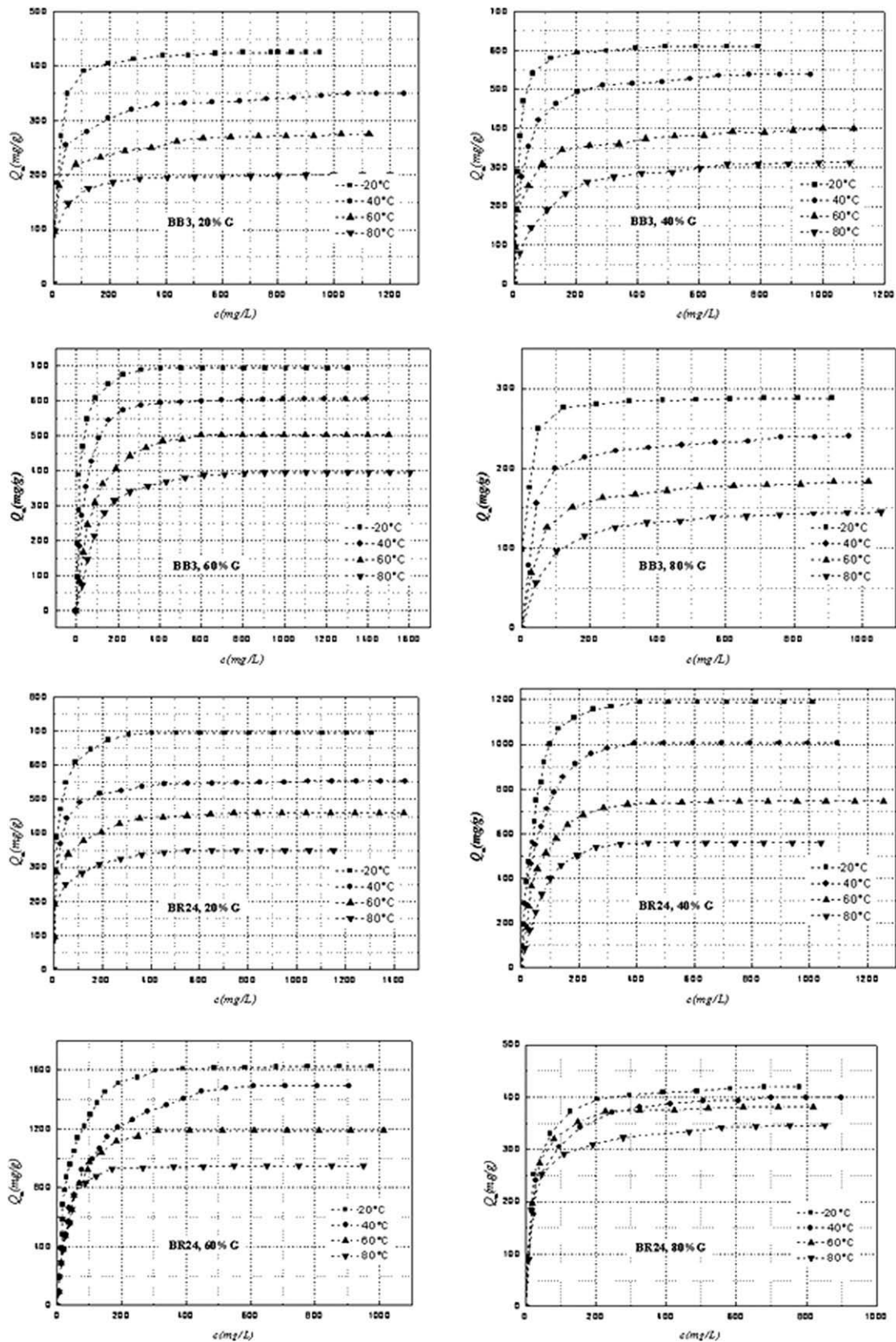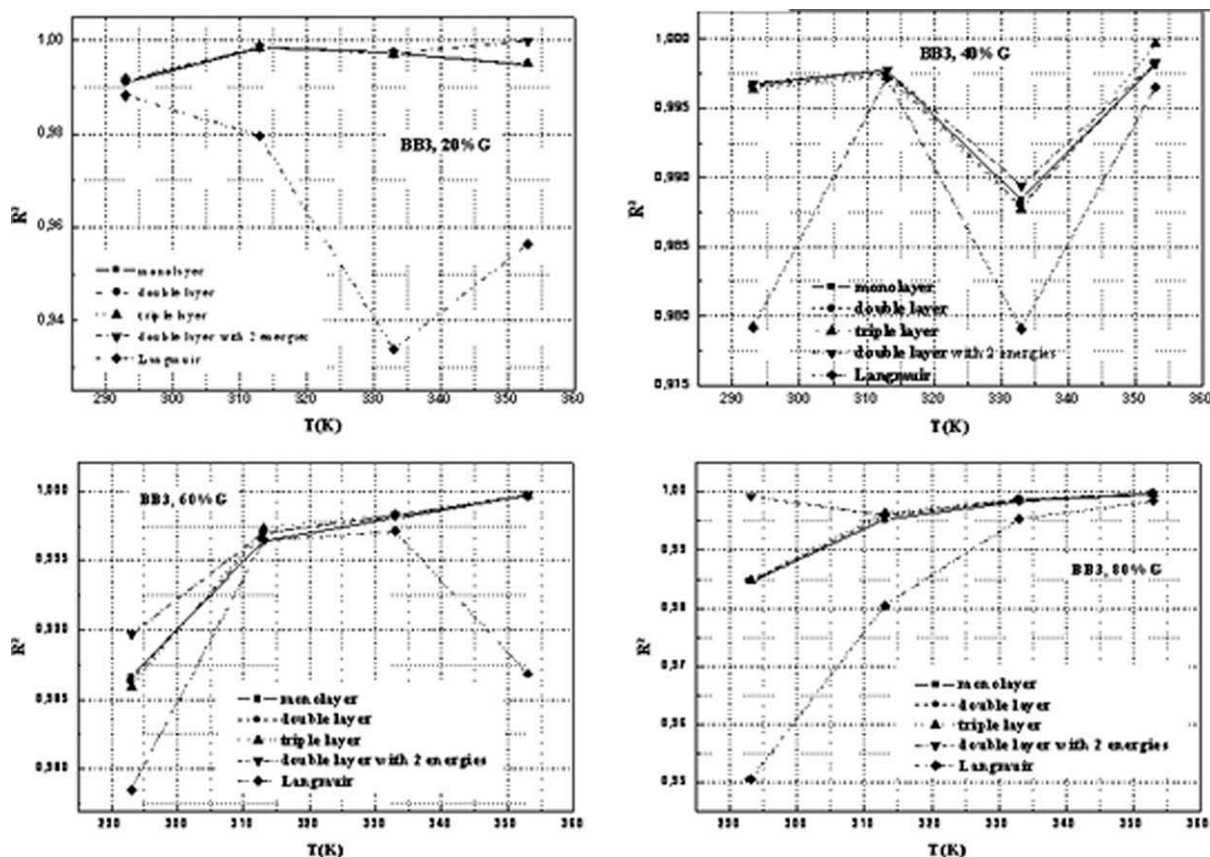
Figure 2 Experimental adsorption isotherms.

Figure 3 Behavior of the correlation coefficient R^2 versus the temperature for different model of the dye molecule BB3.

The adsorbed quantity is written as a function of the dye concentration:

$$Q_a = nN_M \frac{\left(\frac{c}{c_1}\right)^n + 2\left(\frac{c}{c_2}\right)^{2n}}{1 + \left(\frac{c}{c_1}\right)^n + 2\left(\frac{c}{c_2}\right)^{2n}} \tag{3}$$

where n represents the number or fraction of molecule adsorbed onto one receptor site. N_M is the receptor sites density per mass unit. c is the concentration of dye in aqueous solution.

c_1 and c_2 are energetic parameters which can be written as[18]:

$$c_1 = Z_g e^{-\frac{\Delta E_{a1}}{RT}} \quad \text{and} \quad c_2 = Z_g e^{-\frac{\Delta E_{a2}}{RT}} \tag{4}$$

or

$$c_1 = c_s e^{-\frac{\Delta E_1^a}{RT}} \quad \text{and} \quad c_2 = c_s e^{-\frac{\Delta E_2^a}{RT}} \tag{5}$$

where T is the temperature, Z_g is the translational partition function, and c_s is the solubility concentration of the dye. $(-\Delta E_a)$ and $(-\Delta E^a)$ represent the adsorption energies from the hypothetical free state and the dissolved one, respectively.

From eq. (3), it is easy to see that the adsorbed quantity at saturation can be written: $Q_{asat} = 2.n.N_M$

All the numerical values of the model parameters n, N_M, c_1, and c_2 are determined by using a fitting computer program.

After that, it will be easy to determine the evolution of different steric (n, N_M, Q_{asat}) and energetic (c_1 and c_2) parameters versus experimental conditions, namely temperature, in which adsorption occurs.

The advantage to apply this analytical treatment is to give a physical meaning to the parameters involved in the model and then give microscopic characterization from macroscopic measurements. This kind of analysis has a great advantage due to its mathematical and theoretical simplicity.

RESULTS AND DISCUSSION

The objective of this article is to focus on the interpretation of the parameters behavior as a function of the experimental conditions and this is to better understand the adsorption process at microscopic level. Furthermore, the contribution of statistical physics treatment in the investigation of adsorption process will be highlighted.
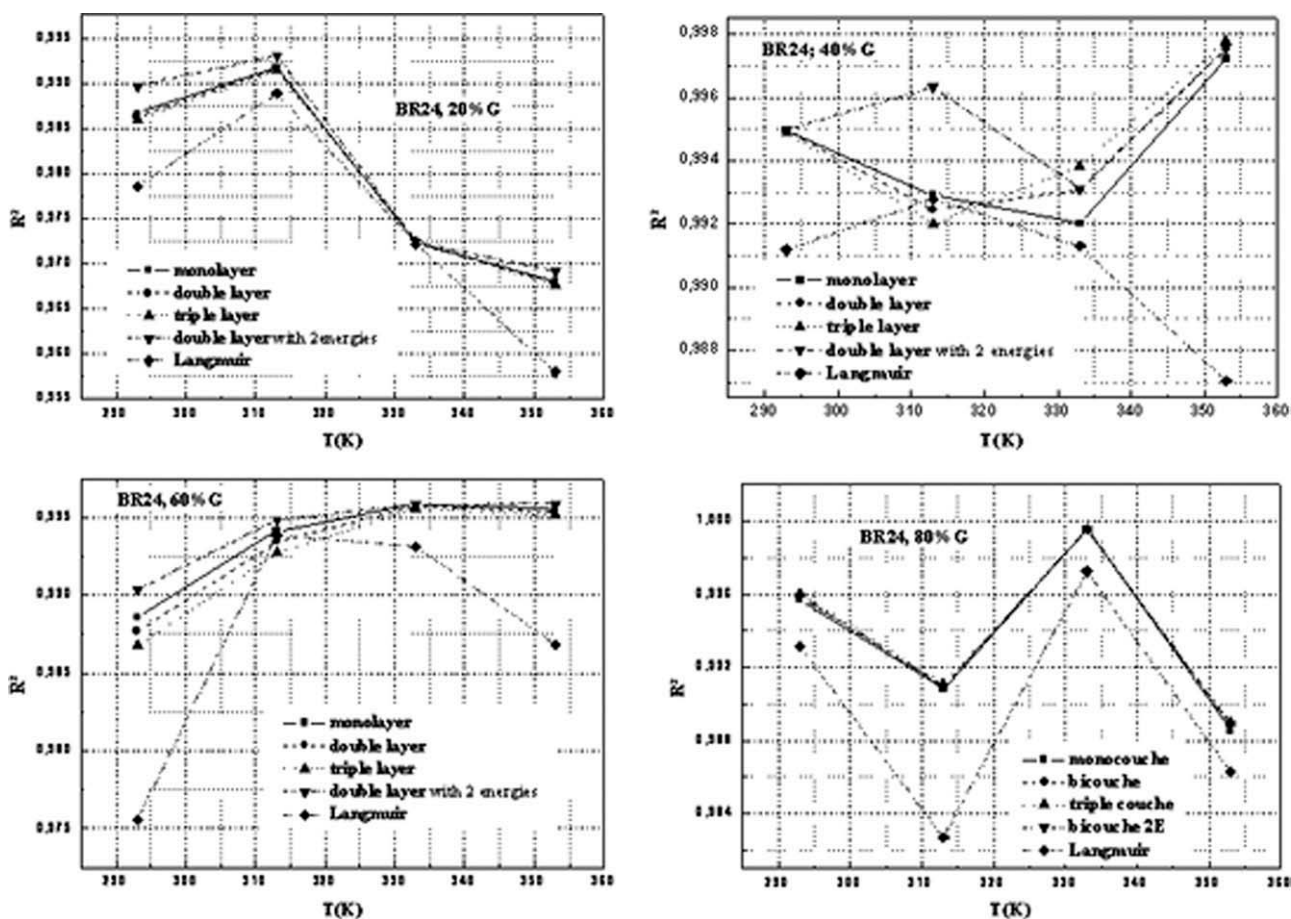
Figure 4 Behavior of the correlation coefficient R^2 versus the temperature for different model of the dye molecule BR24.

Steric parameters

Parameter n

Each of the two studied molecules has only one cationic site. The expected result is therefore the value of n equals 1. But the actual process is not as simple as this. The anchorage number which is defined as $n' = 1/n$ can indicate if the adsorption occurs only with the cationic charge or other types of anchorage can take place.

For BB3, the maximum number of molecule per site is reached at low temperature and at the degrees of grafting of 40, 60, and 80% (Fig. 5). Indeed, the value of n is then superior to the unit and the adsorption process is multimolcules. n exceeds the value 1, this indicates that a polymerization occurs prior to the adsorption process: two or three molecules were adsorbed onto one receptor site. This is due to the relatively weak thermal agitation. Also, the dye molecules are arranged perpendicularly with the cationic charge surface.

At 20% of the grafting degree, the value of n is inferior to the unit at low temperature (till 333 K) and therefore the adsorption is multianchorage. At high temperature, both multianchorage and multimole-

cules processes tend to monomolecule one due to the thermal agitation and collisions. The increase of temperature leads to a rise in thermal collisions. Thus, the aggregation by multimolecules or multianchorage disappears as a consequence of thermal collisions and the anchorage number n' ($= 1/n$) is near to 1. The BB3 molecule is then adsorbed by one site. This dye possesses only one cationic site, so Van der Waals or hydrogen bonds are then necessarily involved at low temperature for 20% of grafted nylon. Furthermore, the delocalization of the cationic charge is promoted by increasing temperature.

For BR24, the parameter n has a maximum value at low temperature and for grafting density of 20 and 60% (Fig. 6). The BR24 molecule is then multimolecules adsorbed and perpendicularly to the surface with its cationic charge. For 40 and 80% of grafted sites, the adsorption process is multianchorage at low temperature. In both cases at high temperature the adsorption tends to be a monomolecule process with its cationic charge due to thermal agitation. This could be explained by the fact that only the cationic interactions occur when the thermal collisions increases.
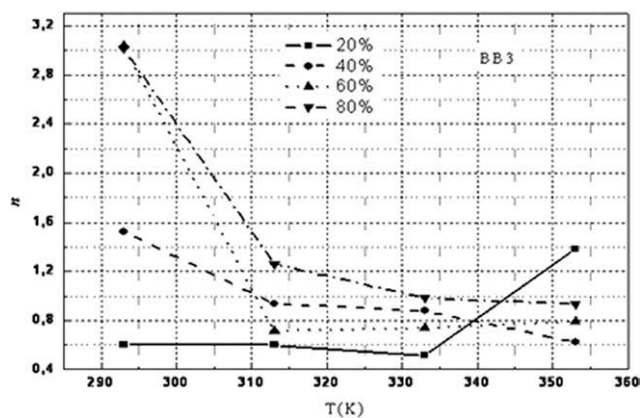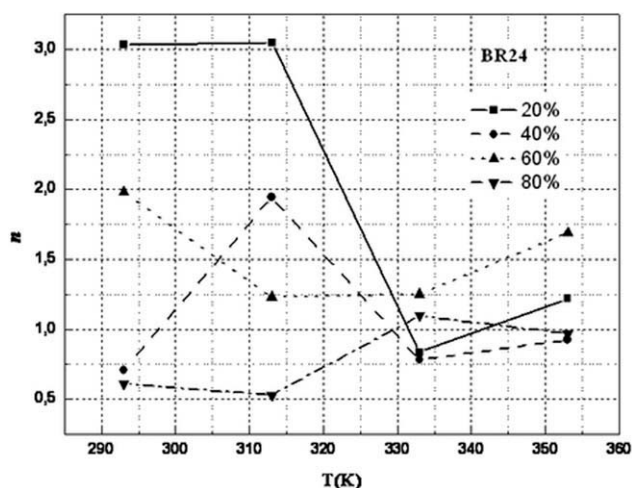
Figure 5 Behavior of the parameter *n* versus the temperature for different degree of grafting in the case of BB3 dye.

As a conclusion, the delocalization of the cationic charge in the case of BB3 is favored by the increase of temperature and the dye molecule seems to have three anchorage active sites. BR24 has only one fixed cationic charge. At low temperature some additional sites such as Van der Waals and hydrogen bonds appeared when the multianchorage adsorption process occurred in the case of 20 and 80%. In the other cases a multimolecules adsorption occurred. At high temperature, only a monomolecule process occurred due to the thermal agitation for all percentages.
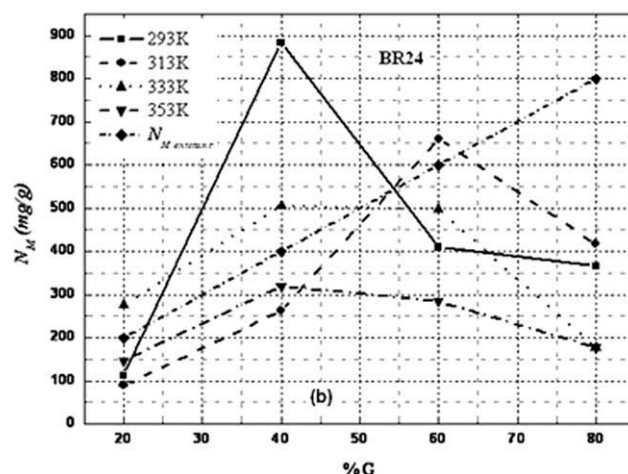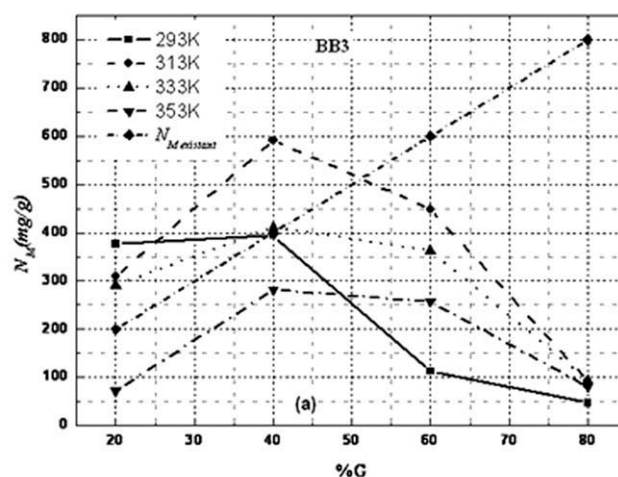
Parameter N_M

N_M is proportional to the adsorption capacity, so its investigation is an indirect method to search the optimum conditions to ameliorate the adsorption capacity. The parameter N_M represents the number of receptor sites density. The values of this parameter determined by fitting of the experimental data

represent the mean density of effectively occupied receptor sites and not the existing (or grafted) ones. Normally, this parameter increases linearly with the grafting rate. However, the obtained values of N_M indicate that such parameter can increase or decrease according to the experimental conditions. In the following, the causes of such variations will be investigated.

From Figure 7a it could be noticed that the number of occupied receptor sites is less than the one of grafted sites except at low temperature. This could be explained by the fact that some receptor sites are not occupied. These results are in good agreement with the fact that the BB3 molecule is anchored perpendicularly to the surface in several molecules per site which has as consequence a steric hindrance. At low temperatures, the inverse phenomenon occurred. This confirms the existence of additional receptor sites due to Van der Waals or hydrogen bonds in addition to the anionic sites, a result that was found by investigation of the parameter *n*.

Figure 6 Behavior of the parameter *n* versus the temperature for different degree of grafting in the case of BR24 dye.

Figure 7 Behavior of the parameter N_M versus degree of grafting for different temperature in the case of BB3 and BR24 dyes.
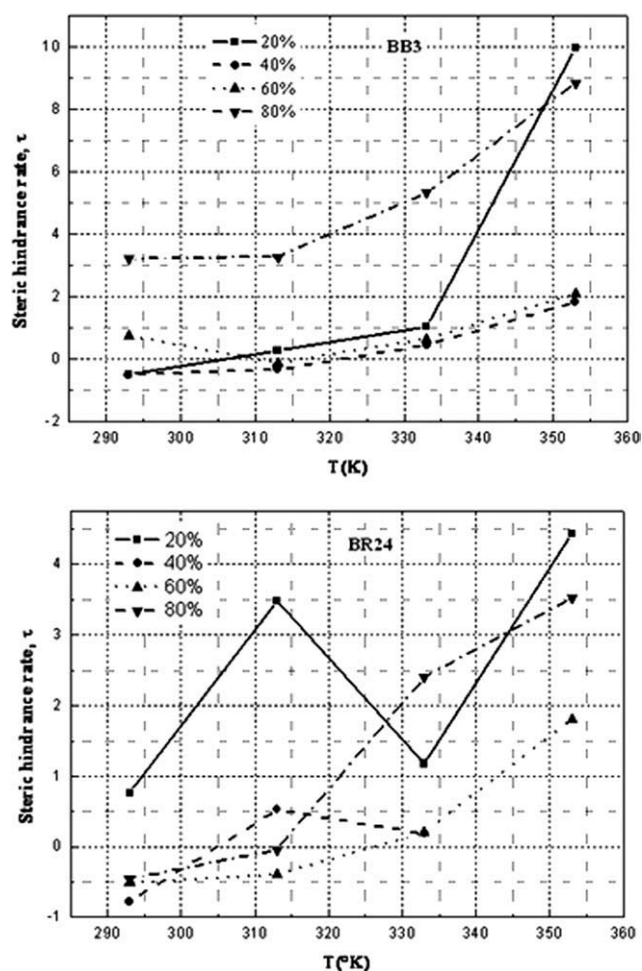
Figure 8 Behavior of the parameter τ versus temperature for different temperature in the case of BB3 and BR24 dyes.

Therefore, the diminution of occupied N_M is followed by an increase of the parameter n (or a diminution of the anchorage number) and a polymerization process appears conveying the steric hindrance. Contrary to BB3 molecule adsorption, Figure 7(b) shows the existence of additional site at high temperature in the case of BR24 adsorption.

Steric hindrance τ

The steric hindrance coefficient τ was defined by the following expression as[16]:

$$\tau = \frac{N_{Mexisting} - N_M}{N_M} \qquad (6)$$

where $N_{Mexisting}$ is the grafted receptor sites density and $(N_{Mexisting} - N_M)$ represents the grafted unoccupied sites.

The unoccupation does not convey a lack of adsorbed molecules but is due to the existence of voluminous molecules that can hide some receptor sites.

The evolution of the steric hindrance in the case of BB3 and BR24 (Fig. 8) shows that the values can be positive, null or negative. The positive values indicate a real steric hindrance. This steric hindrance is probably due to the polymerization of adsorbed molecules. The null values obtained at low temperatures indicate that there is no hindrance when the number of $N_{Mexisting}$ is equal to N_M. This could be explained by the fact that there is an adequation between grafted sites and cationic ones of the dye molecules or that the number of additional receptor sites is equal to the receptor sites hidden. The negative values indicate that N_M is superior to $N_{Mexisting}$. This difference is due to the intervention of Van der Waals and hydrogen bonds. It is then a gain in the adsorption process. So, weak and negative values are searched to optimize the adsorption. The negative values are noticed at low temperatures except for BB3 for high rate grafting and for BR24 at low rate grafting very useful to the adsorption. It could be also noticed that the maximum of steric hindrance is reached at high grafting rate where the receptor
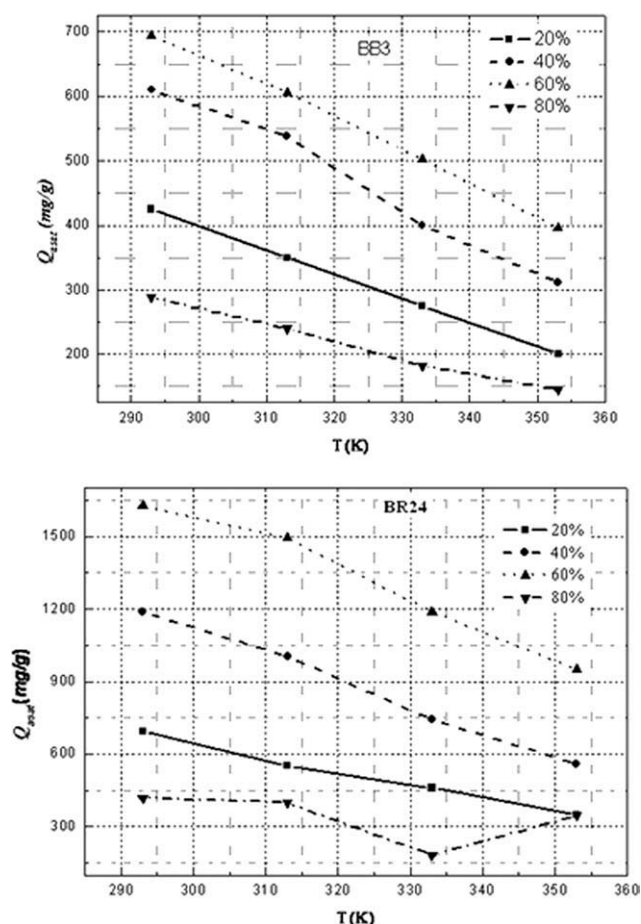
Figure 9 Behavior of the parameter Q_{asat} versus temperature for different %G in the case of BB3 and BR24 dyes.
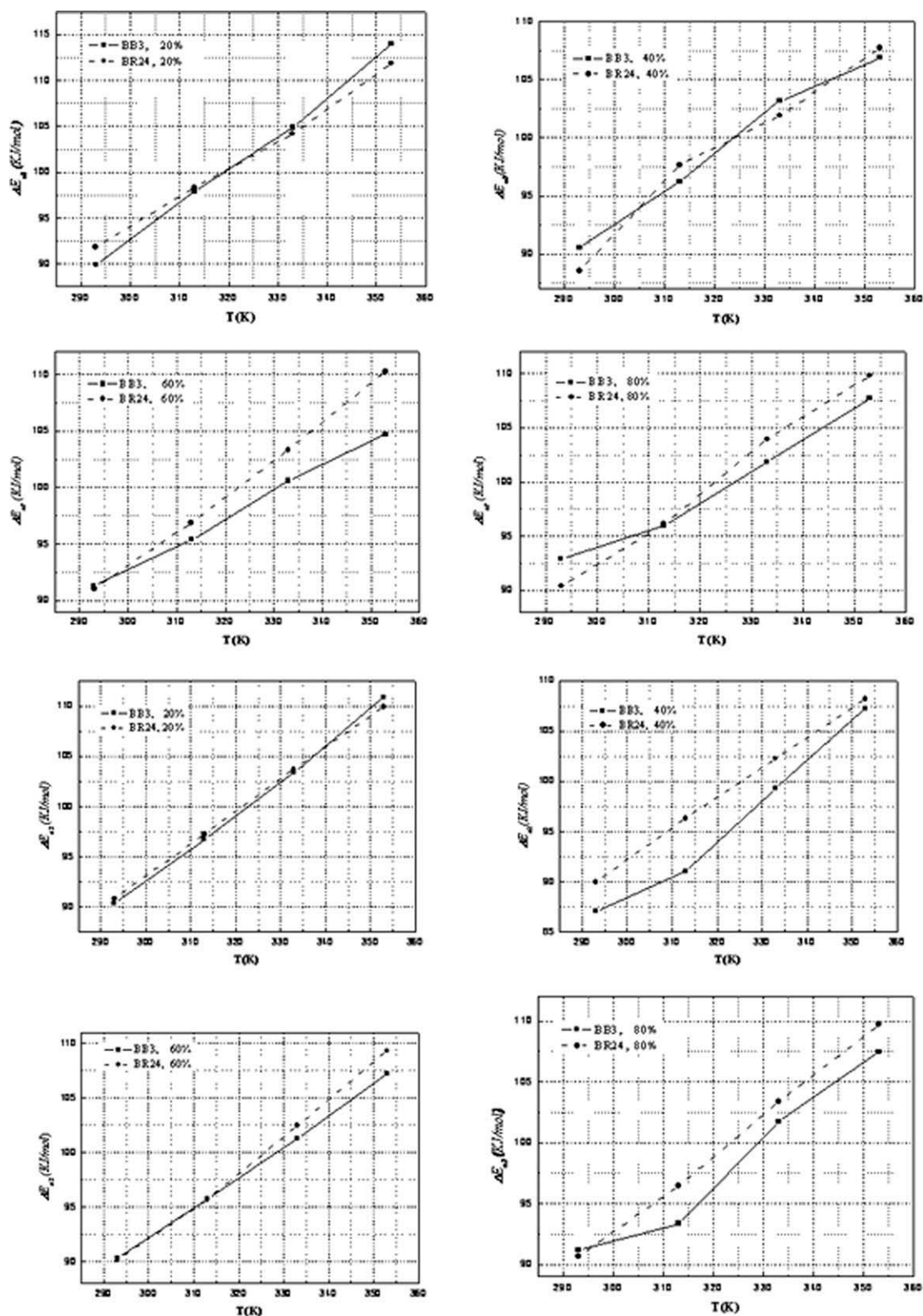
Figure 10 Adsorption energies from the free state versus temperature at the first layer ($-\Delta E_{a1}$) and at the second one ($-\Delta E_{a2}$) for the two dyes BB3 and BR24.

sites are close to each other, so it is better to avoid it. The values of steric hindrance in the case of BB3 is high compared to the ones in the case of BR24

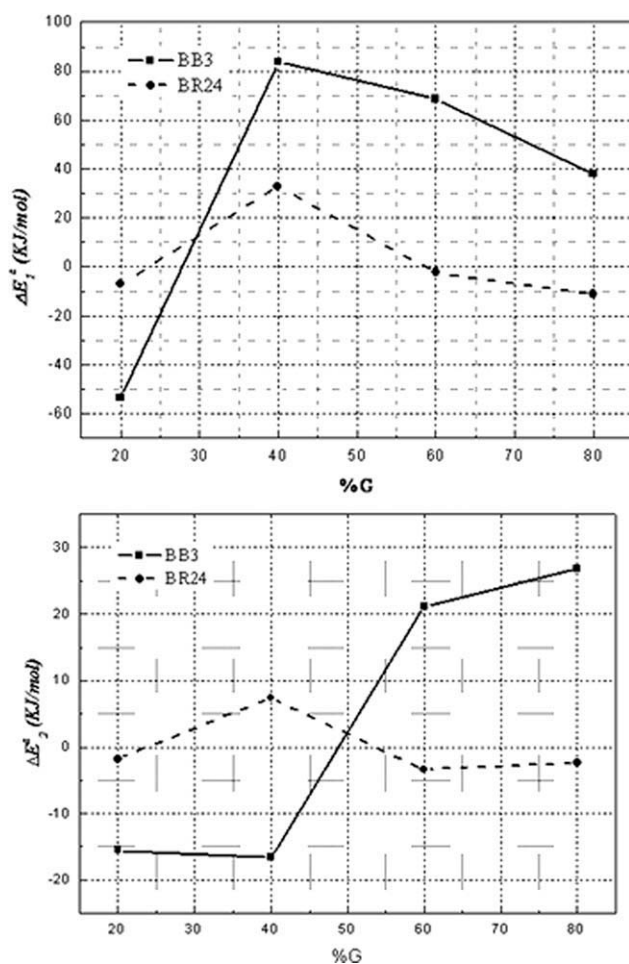and this is probably explained by the fact that BB3 dye has three aromatic rings and BR24 presents only two rings.

Figure 11 Adsorption energies from the dissolved state versus temperature at the first layer ($-\Delta E_1^a$) and at the second one ($-\Delta E_2^a$) for the two dyes BB3 and BR24.

Parameter Q_{asat}

The parameter Q_{asat} represents the adsorbed quantity per gram of MAA-nylon at saturation.

According to the statistical physics treatment, the adsorbed dye quantity at saturation can be written as:

$$Q_{asat} = n.N_M.N_{imax} \quad (7)$$

where N_{imax} represents the maximal number of adsorbed layers (in this study $N_{imax} = 2$).

For BB3 and BR24 dyes, Q_{asat} decreases when the temperature increases (Fig. 9). Indeed, the increase of temperature caused the rise of the thermal collisions and then the molecules cannot be easily fixed onto the adsorbent surface and this may be seen by the decrease of either n or N_M at high temperature (Figs. 5–7). Also, the maximum of adsorbed dye quantity at saturation is reached for a density of grafting of about 60 and 40% with less degree (Fig. 9). If we increase the %G, Q_{asat} decreases (Fig. 9). This may be due to the notable increase of the steric hindrance and the delocalization of charge

in the case of BB3 dye. So, to obtain good waste-water depollution or good dyeing, it is important to operate first of all at low temperature and secondly not to use the grafted nylon over 60%. It is not necessary to lose materials since the adsorption capacity can not increase beyond 60%. It is an important remark in industrial point of view.

From eq. (7), it can be noticed that the increase of the adsorption capacity is affected by the anchorage number, the receptor sites density and also by the number of adsorbed layers. As a conclusion, the optimal conditions to get a high adsorption capacity can be estimated.

Energetic parameters

Both constants c_1 and c_2 are energetic parameters. These parameters are related to the adsorption energy from the hypothetic free state or from the dissolved one [eqs. (4) and (5)].
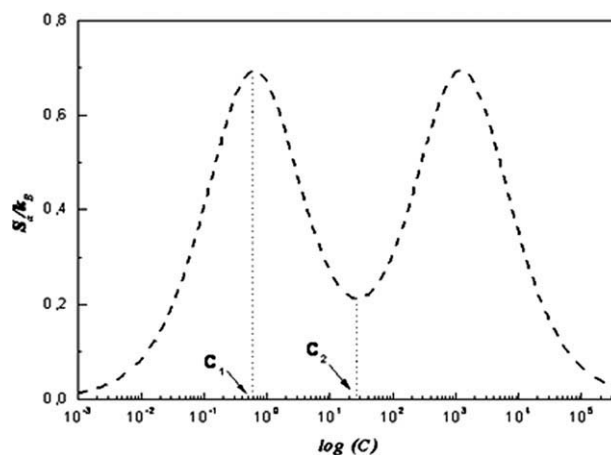
Adsorption energy from free state

Basing on eq. (4) and the value of molar mass of the two studied dyes, it is possible to evaluate the adsorption energies from the free state and this is at each adsorbed layer.

For the BB3, the adsorption energy form the free sate is written as:

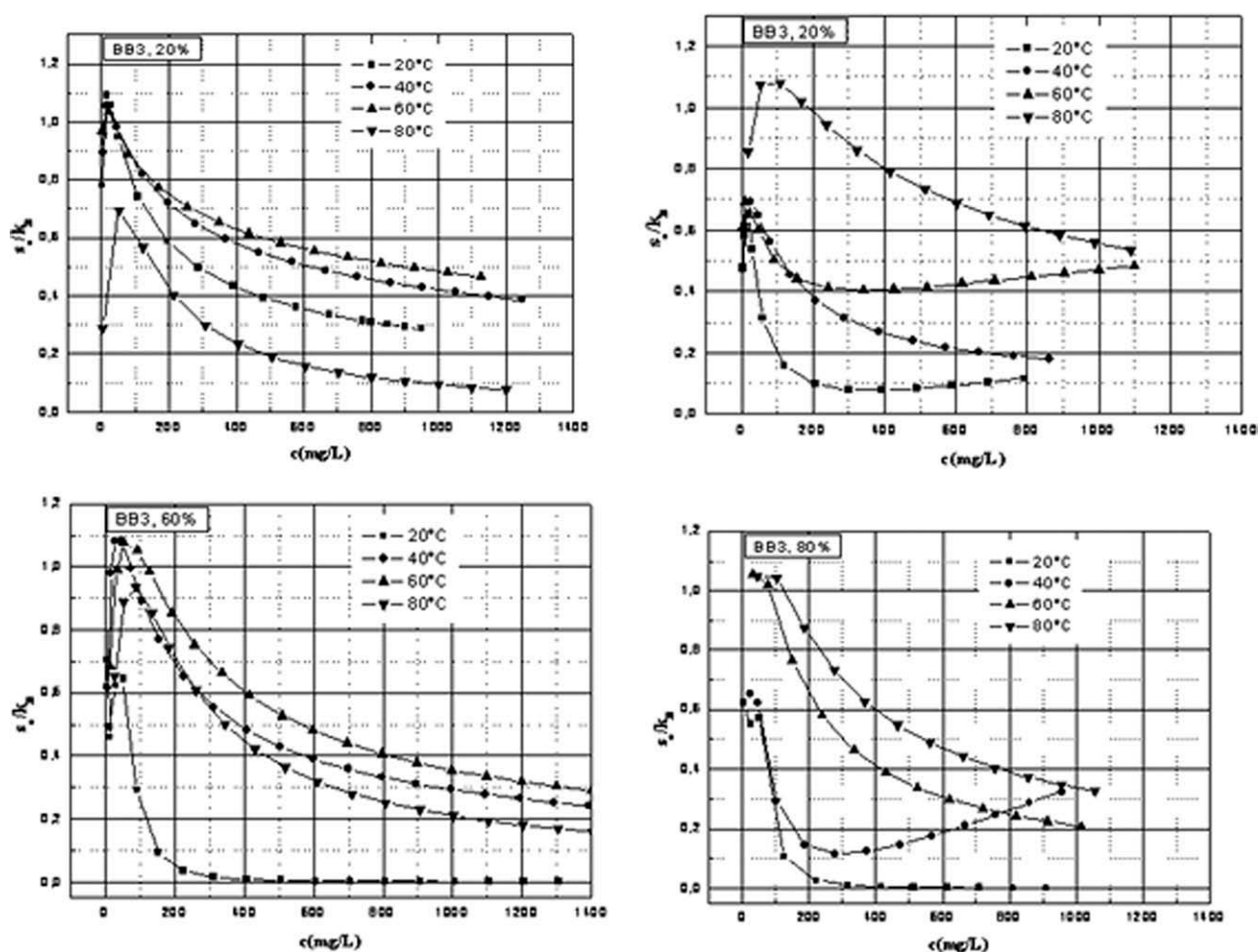$$\Delta E_{a1,2} = 8.314 \ln \left(\frac{c_{1,2}}{4.05 \times 10^{34}} \right) \quad (8)$$

and for BR24, the expression is:

$$\Delta E_{a1,2} = 8.314 \ln \left(\frac{c_{1,2}}{6.48 \times 10^{34}} \right) \quad (9)$$

Figure 12 Evolution of the entropy as a function of adsorbate concentration according to the double layer model with two energy levels with $c_1 = 0.62$, $c_1 = 27.65$, and $n = 0.98$.

Figure 13 Behavior of the entropy versus the adsorbed quantity at four temperatures and four grafted contents for the BB3 dye.

where the index 1 and 2 are related to the first and the second adsorbed layer, respectively.

Figure 10 shows that the value of adsorption energy from free state ($-\Delta E_a$) is always negative and the adsorption process is exothermic. Moreover, adsorption energy increases in modulus with increasing temperature. Indeed, the increase in temperature has a consequence to decrease the distance between active receptor sites and then the surface energy becomes more important.

Adsorption energy from dissolved state

From Figure 11 it could be noticed that the adsorption energy values from dissolved state can be positive or negative. Indeed, when the values of ($-\Delta E^a$) is positive that means the dye molecule takes energy from the solvent to be adsorbed and it is an endothermic adsorption process. In the other case where the adsorption energy is negative, the dye molecule gives energy to the solvent and the process is exothermic.

It could be also noticed that the adsorption energy variations range are more important in the case of BB3. Indeed, BB3 molecule, as it was mentioned before, has a delocalized charge which is affected by the temperature variation. Moreover, at low grafting rate where the distance between receptor sites is important, the adsorption energies are comparable in both cases. This is probably due to the fact that ionic interactions are dominant when adsorption is occurred at the first layer.

At the first layer which is characterized by the adsorption energy ($-\Delta E_1^a$), BB3 dye is much more stable than BR24 one. This could be probably explained by the fact that the delocalized charge of BB3 contributes to its stability where the interaction directly occurred with the anionic sites of MAA-nylon. However, at the second layer the inverse phenomenon occurred and the BR24 molecule is more stable when it is adsorbed since it has only one cationic charge and the repulsion is less important between molecules adsorbed at the second layer and the ones in solution (dissolved state).
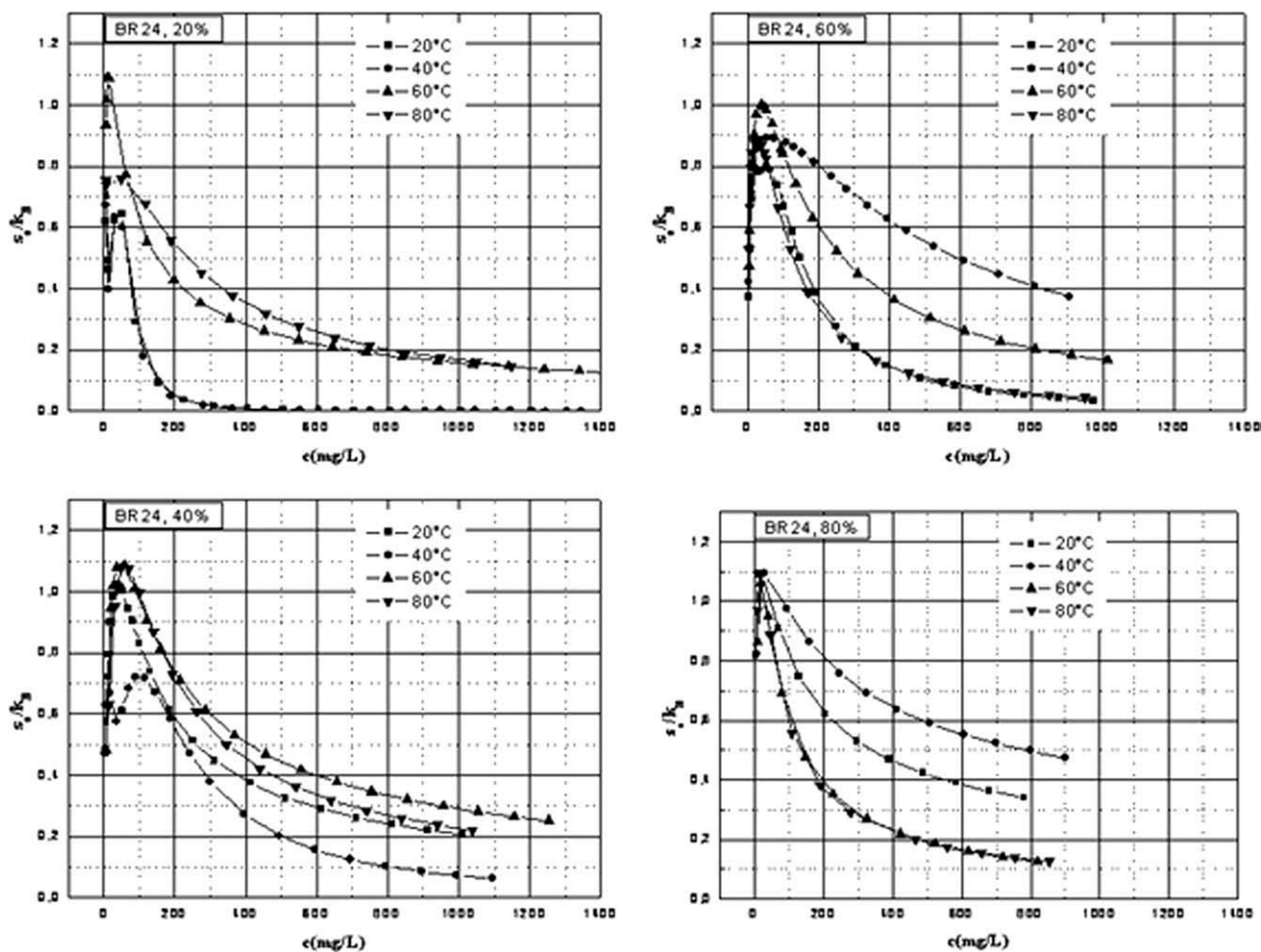
Figure 14 Behavior of the entropy versus the adsorbed quantity at four temperatures and four grafted contents for the BR24 dye.

Adsorption entropy

The information given by the entropy is very important in the characterization of the behavior of adsorbed molecules. In this study, the configurational entropy is considered. This last parameter is due to various arrangements of the adsorbed molecules at the surface. The configurational entropy S_a is deduced from the grand potential J_a as:

$$J_a = -k_B T \ln(Z_{gc}) = E_a - \mu_a Q_a - TS_a \qquad (8)$$

where E_a and Q_a represent the total adsorption energy and the adsorbed quantity, respectively.

eq. (8) can be rewritten as follow:

$$J_a = -\frac{\partial \ln(Z_{gc})}{\partial \beta} - TS_a \qquad (9)$$

Then, the entropy is expressed as follow:

$$\frac{S_a}{k_B} = -\beta \frac{\partial \ln(Z_{gc})}{\partial \beta} + \ln(Z_{gc}) \qquad (10)$$

This last analytical expression shows that starting from the grand canonical partition function it is possible to evaluate the magnitude of the configurational entropy S_a. In the case of the double layer model with two energy levels, the obtained expression of the configurational entropy as a function of the adsorbate concentration is:

$$\frac{S_a}{k_B} = -\left\{ \frac{\left(\frac{c}{c_1}\right)^n \ln\left(\frac{c}{c_1}\right)^n + \left(\frac{c}{c_2}\right)^{2n} \ln\left(\frac{c}{c_2}\right)^{2n}}{1 + \left(\frac{c}{c_1}\right)^n + \left(\frac{c}{c_2}\right)^{2n}} \right\}$$
$$+ \ln\left[1 + \left(\frac{c}{c_1}\right)^n + \left(\frac{c}{c_2}\right)^{2n} \right] \qquad (11)$$

Figure 12 depicts the general evolution of the entropy given by eq. (11). The entropy increases at the beginning of the adsorption indicating the increase of the disorder where the mobility of adsorbates is important. This fact was concluded by many authors.[19–24] The first maximum of entropy is reached when the first layer is half saturated. Then, the entropy decreases when increasing the adsorbed

quantity. The minimum value of entropy different of zero indicates that the order at the adsorbent surface is not total since the adsorption process does not stopped and the second layer starts to be formed. The second increase observed in entropy means that there is a new disorder when the second layer begins to be filled. This disorder decreases till a value towards zero when the saturation is reached.

Figures 13 and 14 represent the evolution of the entropy in case of BB3 and BR24, respectively. It can be noticed that the entropy increases with the adsorbed quantity before the half-saturation and decreases after this particular concentration. This is easy to explain; when the adsorbed quantity is inferior to the half-saturation, the molecule has various possibilities to choose an empty receptor site to be adsorbed and therefore the disorder increases at the surface with the adsorbed quantity. After the half-saturation, the adsorbent molecule has low probability to choose an empty receptor site since the surface tends toward the saturation and therefore tends toward the order. The observed minimum of entropy nonzero indicates that before the first layer is totally filled, the second one starts to be formed. After that, the same behavior of entropy can be noticed since the first layer is used as adsorbent sites for the second. The entropy can reach zero when the saturation is reached. Normally, for a fixed adsorbed quantity, the higher the temperature is the higher the entropy is since the thermal collisions increases the disorder at the adsorbent surface. However, in the cases of BB3 and BR24 this physical phenomenon is not clearly illustrated and this is due to the more complicated physical process of adsorption of such dyes.

CONCLUSION

In conclusion, a double layer adsorption model with two energy levels has been used to model the BB3 and BR24 adsorption. It is established using the grand canonical partition function. This model leads to better understanding and interpretation the adsorption processes for two basic dyes, BB3 and BR24, onto modified nylon. The parameter n gives an idea on the adsorbed molecule position when changing the experimental conditions. The study of the parameter N_M confirms the existence of additional Van der Walls or hydrogen sites. These results were also obtained by studying the parameter n. The τ parameter showed that the steric hindrance of BB3 is more important than BR24 and this was attributed to the size and the shape of adsorbed molecules. Optimal conditions for best adsorption capacity were obtained thanks to the investigation of the evolution of the parameter Q_{asat}. The study of energetic parameters allows us to deduce that BB3 molecule is

more stable at first layer than BR24; whereas at the second layer, the inverse phenomenon occurs. That is due to the localized and the delocalized positive charge. The disorder of the adsorbent surface was studied as a function of adsorbed quantity thanks to the configugational entropy.

In summary, the idea to develop theoretical model based on statistical physics treatment shows a powerful method. It allows to characterize the surface at microscopic level by using macroscopic results, such as adsorption isotherm curves, without any destruction of the system.

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