Adsorption of The Polymer On a Clay Matrix: Theoretical Study

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Abstract: Adsorption of polymers is a phenomenon of great importance in a number of areas of our daily life. However, understanding this phenomenon is essential. This work focuses on the theoretical study of the polyethylene glycol (PEG) adsorption phenomenon on the natural clay-layer surface. Clay is considered as a matrix. Different adsorption regimes have been presented. The expressions of the surface coverage ratio as a function of the volume fraction of monomer for each regime were calculated. A strong adsorption was noted for the first two regimes (dilute surface, and bidimensional semi-dilute surface) confirmed by the exponential term. When the surface becomes saturated, we are in the plateau regime for which the adsorption varies logarithmically, due to the occupation of most of the sites available on the clay-layer surface. Finally, we presented the variation of the volume fraction as a function of z (axis perpendicular to the surface), we have shown that a layer of polyethylene glycol (PEG) adsorbed on a natural clay-layer surface is composed of three zones (proximal, central and distal) with different volume fractions.

Keywords: Adsorption, polymers scaling theory, dilute regime, plateau regime, bidimensional semi-dilute surface regime

1. Introduction

The adsorption of polymers has long been the subject of several theoretical studies with the aim of understanding the phenomenon and developing new theoretical approaches. Among these approaches, we cite the mean-field theory, developed by Edwards, but the disadvantage is that it does not take into account the interactions between the monomers which give results very far from the experimental reality. The theory based on the scaling law proposed by authors in [1] has made it possible to take into account these interactions as well as the effects of the solvent. It was also noted that this theory has succeeded in deriving equations which show a good agreement with experience [2].

The very important role of polymers in the formation of protective layers allowing the stabilization of colloidal suspensions and their very important applications specially motivated the search for theoretical approaches to the phenomenon of adsorption and proposed realistic models leading to the reduction of the gap between theory and experience [2]-[4]. On the other hand, the structure of the minerals is multiscale; the size of the agglomerates being of the order of the micrometer, while an individual layer has a thickness close to the nanometer. In the broadest sense, clays and clay minerals are more or less hydrated alumino-silicates belonging to the family of phyllo-silicates, consisting of two-dimensional infinite sheets (Fig.1) [5]. Sometimes the efficiency of these minerals remains insufficient to obtain materials corresponding to the required criteria, which has prompted researchers to test the intercalation of polymers inside the clay sheets as powerful tools in a series of applications such as drilling wells, paints, drug delivery systems, construction and cosmetics [6]-[8]. The most investigated polymers are polyethylene oxide (PEO) and polyethylene glycol (PEG), due to their chemical and thermal stability, relatively low cost, low toxicity, biodegradability as well as

their high adsorption capacity on clay sheets through a strong hydrogen bonding between the oxygen groups of PEG and the hydroxyl groups of clay [9]-[15].

The study presented here is only a small contribution to the growing understanding of polymer adsorption. We will focus more specifically on the reversible adsorption of neutral and flexible polymers, such as polyethylene glycol (PEG), on a given natural clay-layer surface, assumed to be plane, attractive and impenetrable, from a polymer solution in the case of good solvent.

In a polymer solution of finite concentration, the interaction between the different polymers must be taken into account, therefore there are three concentration regimes (diluted, semi-diluted and concentrated) [16]. We focus our effort on understanding the diluted volume regime in which we discuss the ideal case of a single chain and the adsorption isotherms of the three important surface regimes (diluted regime at the surface, semi-diluted two-dimensional regime at the surface, and plateau regime). The volume fraction $\varphi(z)$ at a distance z from the surface and the surface coverage rate Γ were calculated for each regime based on the De Gennes scaling laws theory.

The theory of the scaling laws is an approach, which gives a good qualitative description of the adsorbed layer. However, it does not take into account the concentration correlations induced by the effects of excluded volume but it does take into account the good scale dependencies.

To theoretically study the adsorption on a flat surface of polymers in dilute solution and we propose a model of blobs, which presents an intermediate character between the self-similar adsorbed layer and the grafted layer.
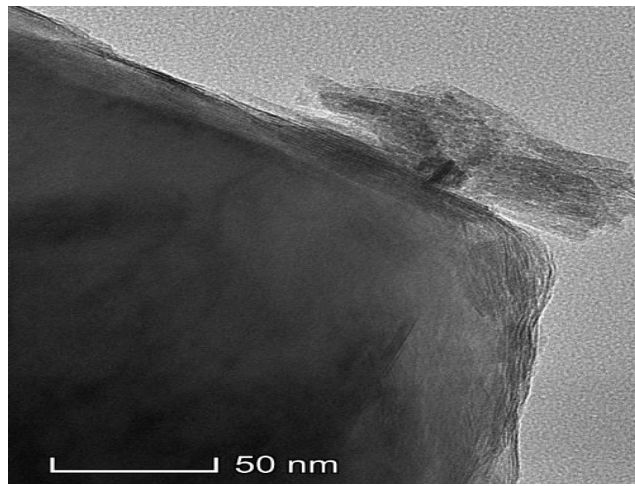

Fig. 1 - Micrographs obtained by transmission electron microscopy for the natural clay from Meknes

2. Dilute Bulk Regime

In this regime, the polymer chains are distant from each other (no mutual interactions) and develop the same conformation as when they are alone in solution (Fig.2). The regime diluted in volume appeared for a volume fraction φ lower than a threshold fraction φ^* ($\varphi < \varphi^*$), from which the individual chains begin to overlap [17].

The estimation of this threshold fraction has not been precisely defined in the literature and its value differs according to the hypothesis of transition from one regime to another. Indeed, the average concentration of monomer inside a chain of radius $R \sim a\,N^\nu$ is given by [1] ;

$$C^* \sim \frac{N}{R^3} \sim a^{-3} N^{1-3\nu} \qquad (1)$$

with N, the degree of polymerization of the chains and at the size of a monomer unit, ν is an exponent as a function of the dimension of the space d and of the solvent, $\nu = 3/(d+2)$.

According to equation (1) we deduce the critical volume fraction of recovery given by:

$$\varphi^* = a^3 C^* \qquad (2)$$

with C^*, represents the volume concentration of monomer. Which gives us:

$$\varphi^* \sim N^{1-3\nu} \qquad (3)$$

In the case of three dimensions, we write:

$$\varphi^* \sim N^{-4/5} \qquad (4)$$

So when the volume fraction in monomer ($\varphi < \varphi^*$), the polymer chains are independent, and they can be considered as single isolated chains (Fig.2), hence the importance of studying the behavior of an isolated chain at neighborhood of an attractive surface.
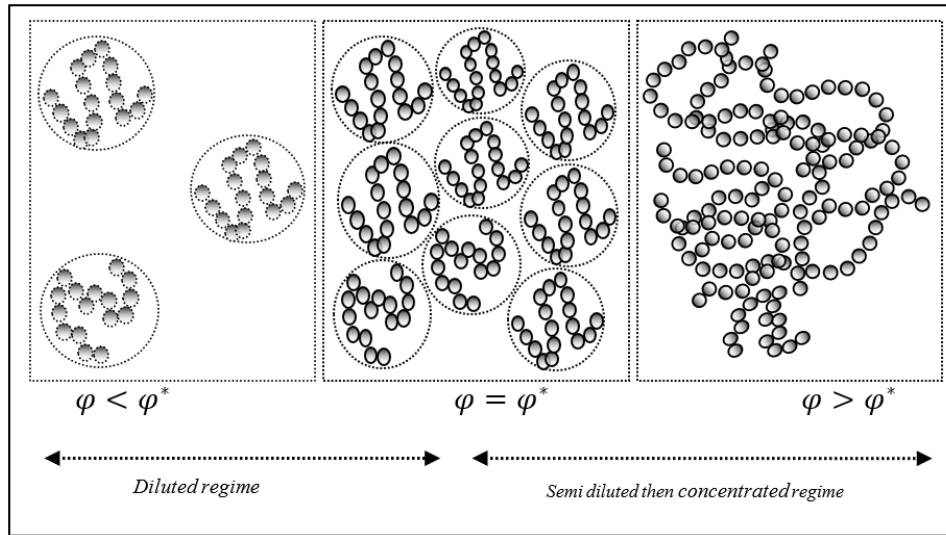

Fig. 2 - Schematic illustration of PEG-chains at different concentration regimes.

2.1 Single PEG-Chain

The single chain is considered to be the simplest problem, and it has been addressed by several authors in [18][19]. Consider a single PEG-chain of polymer in a good solvent in the vicinity of a supposedly plane and impenetrable surface of a natural clay-layer. The estimation of the properties of the single chain was carried out by Flory using Gaussian statistics and the thermodynamics of the mean field gives the following formula:

$$R \sim a\, N^{3/(d+2)}$$

This estimate of the radius of the chain is called the Flory radius. In three dimensions we write:
$$R_F \sim a\, N^{3/5} \qquad (5)$$

In addition, each monomer on the surface is supposed to obtain an attractive energy ($-k_B T \delta$) which promotes the adsorption phenomenon. With k_B is the Boltzmann constant and T is the absolute temperature. In fact, the adsorption takes place above a coupling threshold value defined by [20]:
$$\delta_c \sim N^{-3/5} \qquad (6)$$

Two cases are then discussed:

When $\delta < \delta_c$, the entropic effects dominate and the conformation of the polymer (PEG) is basically isotropic . The dimensions of the chain parallel and orthogonal to the surface remain of the same order as the radius of Flory $R_F \sim a N^{3/5}$ [21], in this case there is a weak adsorption (Fig.3).
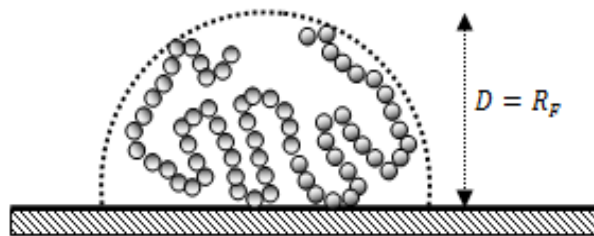

Fig. 3 - Weak adsorption of a single PEG-chain.

On the other hand, for $\delta > \delta_c$, the PEG-chain is adsorbed and expands on the surface, in this case we are talking about polymer blobs rather than chain (Fig.4) [20][21]. To properly define these blobs, it is necessary to determine the two important characteristics which are the thickness of the layer D, and the parallel extension of the Chain $R_\parallel$, by scaling laws.

For the determination of the first characteristic of the blobs, it is assumed that the thickness of the layer takes the form:

$$D = R_F \, f(\delta N^\sigma) \qquad (7)$$

Where $f(x)$ is an unknown function which may be expanded in x for small x, and $f(x = 0) = 1$. In the adsorbed regime $\gg 1$, $f(x)$ has power law behaviour $f(x) = x^{\alpha_1}$, according to equation (7) we write:

$$D = R_F \, (\delta N^\sigma)^{\alpha_1}$$

By Replacing R_F with its expression (5), This leads to

$$D = a \, N^{3/5} \delta^{\alpha_1} N^{\sigma \alpha_1} = a \, \delta^{\alpha_1} N^{\frac{3}{5} + \sigma \alpha_1} \qquad (8)$$

Noting that D should be independent of N and should depend only on δ, so we write according to (7)

$$\frac{3}{5} + \sigma \alpha_1 = 0$$

with $\sigma = 3/5$. We get $\alpha_1 = -1$ and we replace in (8), hence the value of D in the form

$$D \sim a \, \delta^{-1} \qquad (9)$$

Likewise, the second characteristic $R_\parallel$ is calculated in the same way by the application of the scaling law. First suppose that:

$$R_\parallel \sim N^{3/5} \, a \, f(\delta N^{3/5}) \qquad (10)$$

In the case of adsorption, $\delta N^{\frac{3}{5}} \gg 1$ and $f(x) = x^{\alpha_2}$. Equation (10) becomes:

$$R_\parallel \sim N^{3/5} \, a \, \delta^{\alpha_2} \, N^{(3/5)\alpha_2} \sim a \, \delta^{\alpha_2} \, N^{(3/5)\alpha_2 + 3/5} \qquad (11)$$

According to [21] the parallel radius is two-dimensional:

$$R_\parallel \sim a N^{3/4} \qquad (12)$$

The combination of (11) and (12) gives:

$$(3/5)\alpha_2 + 3/5 = 3/4$$

Then $\alpha_2 = 1/4$. Let us replace α_2, in (11) we obtain the relation of the parallel extension of the blob:

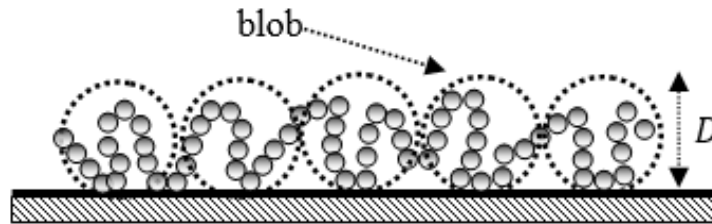$$R_\parallel \sim a \, N^{3/4} \delta^{1/4} \qquad (13)$$

Fig. 4 - Strong adsorption of a single PEG-chain on a surface.

2.2 The Adsorption Isotherms

In this part, we are interested in the calculation of the surface coverage Γ as a function of the volume fraction φ, and in the variation of the volume fraction φ as a function of z which represents the direction orthogonal to the surface.

2.2.1 Surface Diluted Regime

The free energy F per chain is written:

$$F = F_{conf} + F_{att} + F_{trans} \qquad (14)$$

$$\frac{F}{k_B T} = N \left(\frac{a}{D}\right)^{5/3} - N \left(\frac{a}{D}\right)^{2/3} + \frac{F_{trans}}{k_B T} \qquad (15)$$

With, F_{conf} confinement energy, F_{trans}, translation energy and F_{att} the attraction energy.

The minimization of equation (15) with respect to D allows us to find the relation (9):

$$D \sim a\, \delta^{-1}$$

According to [20], the minimized free energy leads to the relationship of the surface chemical potential of the form:

$$\frac{\mu_s}{k_B T} \sim -N\delta^{5/3} + \ln\left(\frac{\Gamma a}{ND}\right) \qquad (16)$$

The equation for the bulk chemical potential writes:

$$\frac{\mu_b}{k_B T} \sim \ln\left(\frac{\varphi}{N}\right) \qquad (17)$$

According to (16) et (17) :

$$\ln\left(\frac{\varphi}{N}\right) = \ln(2) - N\delta^{5/3} + \ln\left(\frac{\Gamma a}{ND}\right)$$

Infers that

$$\Gamma(\varphi) = \frac{1}{2}(D/a)\,\varphi\, e^{N\delta^{5/3}} = \frac{1}{2}\,\delta^{-1}\,\varphi\, e^{N\delta^{5/3}} \qquad (18)$$

This relationship shows that the surface coverage is proportional to the volume fraction φ. In addition, the surface layer is diluted as long as Γ less than a critical fraction Γ_1:

$$\Gamma_1 = \frac{1}{2}\frac{Na^2}{R_\parallel^2}$$

With, $R_\parallel \sim a\, N^{3/4}\delta^{1/4}$:

$$\Gamma_1 = \frac{1}{2}N^{-1/2}\,\delta^{-1/2} \qquad (19)$$

When $\Gamma(\varphi_1) \sim \Gamma_1$, we can write $\frac{1}{2}\delta^{-1}\varphi_1 e^{N\delta^{5/3}} = \frac{1}{2}N^{-1/2}\delta^{-1/2}$, so we deduce the critical volume fraction :

$$\varphi_1 = N^{-1/2}\,\delta^{1/2}\,e^{-N\delta^{5/3}} \qquad (20)$$

2.2.2 Two-dimensional Semi-Diluted Surface Regime

When the surface coverage increases and becomes greater than the critical value Γ_1 ($\Gamma > \Gamma_1$) the surface layer is in the two-dimensional semi-diluted regime but the volume is always in the diluted regime. The adsorbed macromolecules interact strongly with each other. The characteristic dimensions of the blobs in this regime are calculated using the scaling laws. For the parallel extension $R_\parallel$ we write the formula:

$$R_\parallel \sim a\, N^{3/4}\,\delta^{1/4}\, f(\Gamma/\Gamma_1) \qquad (21)$$

For the case $\Gamma > \Gamma_1$, we have:

$$R_\parallel \sim a\, N^{3/4}\,\delta^{1/4}\,(\Gamma/\Gamma_1)^{\alpha_3} \sim a\, N^{3/4}\,\delta^{1/4}\,\left(\Gamma\, N^{1/2}\,\delta^{1/2}\right)^{\alpha_3}$$

In the semi-diluted range, we require that the radius behave like $N^{1/2}$ so:

$$a\, N^{3/4}\,\delta^{1/4}\left(\Gamma\, N^{1/2}\,\delta^{1/2}\right)^{\alpha_3} \sim N^{1/2}$$

This leads to $\alpha_3 = -1/2$, equation (21) becomes $R_\parallel \sim a\, N^{3/4}\,\delta^{1/4}\left(\Gamma\, N^{1/2}\,\delta^{1/2}\right)^{-1/2}$, finally $R_\parallel \sim a\, N^{1/2}\,\Gamma^{-1/2}$

Following the same calculation For $\xi_\parallel$, defined by:

$$\xi_\parallel \sim a\, N^{3/4}\,\delta^{1/4}\, f(\Gamma/\Gamma_1) \qquad (22)$$

So, $\xi_\parallel \sim a\, N^{3/4}\,\delta^{1/4}\,(\Gamma/\Gamma_1)^{\alpha_4} \sim a\, N^{3/4}\,\delta^{1/4}\left(\Gamma\, N^{1/2}\,\delta^{1/2}\right)^{\alpha_4}$, assuming that $\xi_\parallel$ is independent of N, this leads to $\alpha_4 = -3/2$

Equation (22) becomes:

$$\xi_\parallel \sim a\, \delta^{-1/2}\,\Gamma^{-3/2} \qquad (23)$$

Regarding $R_\perp$ we assume that

$$R_\perp \sim D\, f(\Gamma/\Gamma_1) \qquad (24)$$

For $> \Gamma_1$, we write

$$R_\perp \sim D\left(\Gamma\, N^{1/2}\,\delta^{1/2}\right)^{\alpha_5} \qquad (25)$$

Suppose that in the case of a semi-dilute regime the radius varies as $N^{3/5}$, therefore according to equation (25):

$$D\left(\Gamma\, N^{1/2}\,\delta^{1/2}\right)^{\alpha_5} \sim N^{3/5}$$

From where, $\frac{1}{2}\alpha_5 = 3/5$ so $\alpha_5 = 6/5$, and equation (25) becomes :

$$R_\perp \sim a \, N^{3/5} \left(\Gamma \, \delta^{-1/3} \right)^{6/5} \qquad (26)$$

Let's compare the equation $D \sim a \, \delta^{-1}$ with $\xi_\parallel \sim \delta^{-1/2} \, \Gamma^{-3/2}$, so we get $\Gamma_2 \sim \delta^{1/3}$. So that $\xi_\parallel$ be greater than D, surface coverage must be less than critical coverage Γ_2.

Let us evaluate, now the two free energies, of confinement F_{conf} and repulsive F_{rep} which are given respectively by:

$$\frac{F_{conf}}{kT} \sim N \left(\frac{a}{D} \right)^{5/3} \qquad (27)$$

$$\frac{F_{rep}}{kT} \sim \frac{N}{g_\parallel} \qquad (28)$$

With, $g_\parallel$ represents the number of monomers per blob.

By analogy with equation (13) $R_\parallel \sim a \, N^{3/4} \, \delta^{1/4}$ and assuming that the blob behaves like a single chain we can write:

$$\xi_\parallel \sim a \, g_\parallel^{3/4} \delta^{1/4} \qquad (29)$$

Compare the equation $\xi_\parallel \sim a \, \delta^{\frac{-1}{2}} \, \Gamma^{-3/2}$, with equation (29), we write

$$a \, \delta^{\frac{-1}{2}} \, \Gamma^{-3/2} \sim a \, g_\parallel^{3/4} \delta^{1/4} \ ,$$

this leads to

$$g_\parallel \sim \delta^{-1} \, \Gamma^{-2}$$

Then equation (28) becomes:

$$\frac{F_{rep}}{kT} \sim N \delta \Gamma^2 \qquad (30)$$

According to equations (9), (27) and (30) we write:

$$\frac{F_{rep}}{F_{conf}} \sim \delta^{-2/3} \Gamma^2$$

As long as, the surface fraction Γ lower than a critical surface fraction $\Gamma_2 = \frac{1}{2} \delta^{1/3}$, we can neglect the repulsive free energy compared to the confining energy. This implies that the coverage area for the semi-diluted two-dimensional surface regime is the same as in the diluted surface regime given in equation (18).

$$\Gamma = \frac{1}{2} \delta^{-1} \varphi \, e^{N \delta^{5/3}}$$

To determine the critical volume fraction of this regime, we assume that $\Gamma_2 = \Gamma(\varphi_2) = \frac{1}{2} \delta^{1/3}$, therefore $\delta^{-1} \varphi_2 \, e^{N \delta^{5/3}} = \delta^{1/3}$. This leads to

$$\varphi_2 = \delta^{4/3} \, e^{-N \delta^{5/3}} \qquad (31)$$

Therefore, the semi-diluted two-dimensional regime on the surface is defined in the interval $\varphi_1 \ll \varphi \ll \varphi_2$ for the volume fraction and in the interval $\Gamma_1 \ll \Gamma \ll \Gamma_2$ for the coverage rate of the surface.

2.2.3 Two-dimensional Semi-Diluted Surface Regime

When the coverage rate of the surface Γ becomes greater than the critical value Γ_2, we cannot neglect the repulsive energy as discussed in the previous section. In addition, the size of blobs $\xi_\parallel$ becomes of the same order of magnitude as D. Free energy is therefore written

$$F = F_{conf} + F_{att} + F_{rep} + F_{trans} \qquad (32)$$

$$\frac{F}{k_B T} = N \left(\frac{a}{D} \right)^{5/3} - N \left(\frac{a}{D} \right)^{\frac{2}{3}} \delta + N \Gamma^2 \, \delta + \frac{F_{trans}}{k_B T} \qquad (33)$$

Where the first, the second and the third terms are respectively the confinement, the attractive and the repulsive interaction energy per chain. The last term corresponds to the translation of the center of mass. Minimization of F with respect to D, leads to $D \sim (a/\delta)$. The minimized free energy

$$\frac{F}{k_B T} \sim - N \, \delta^{5/3} + N \, \Gamma^2 \, \delta + \frac{F_{trans}}{k_B T}$$

Which gives $\Gamma \sim \delta^{1/3}$, this corresponds to the case of the plateau regime for which the coverage rate of the surface Γ becomes independent of the fraction φ in volume and the surface becomes saturated.

According to equations (16) and (33), we deduce the surface chemical potential

$$\mu_s = ln \left(\frac{\Gamma a}{ND} \right) - N \delta^{5/3} + N \, \Gamma^2 \delta \ . \qquad (34)$$

By comparing the surface chemical potential and the volume chemical potential given by

$$\frac{\mu_b}{k_B T} \sim \ln \left(\frac{\varphi}{N} \right) , \qquad (35)$$

we can deduce the correction for the coverage rate of the surface we write then

$$\Gamma = \delta^{1/3}(1 + \varepsilon) \quad \text{with} \quad \varepsilon \ll 1 \tag{36}$$

The equality of the two potentials $\mu_b \sim \mu_s$, gives :

$$ln\left(\frac{\Gamma a}{ND}\right) - N\delta^{5/3} + N\Gamma^2\delta \sim ln(\frac{\varphi}{N})$$

$$ln(\Gamma) + N\Gamma^2\delta \sim ln\left(\frac{\varphi D}{a}\right) + N\delta^{5/3}$$

$$ln(\Gamma) + N\Gamma^2\delta \sim ln\left(\frac{D}{a}\varphi\right) + N\delta^{5/3} \tag{37}$$

In the relation (37), we replace Γ by the following expression $\Gamma = \delta^{1/3}(1 + \varepsilon)$

$$ln(1 + \varepsilon) + N\delta^{5/3}(1 + \varepsilon)^2 \sim ln(\varphi\delta^{-4/3}) + N\delta^{5/3}$$

Also for $\ll 1$:

$$ln(1 + \varepsilon) = \varepsilon \quad et \quad (1 + \varepsilon)^2 = 1 + 2\varepsilon$$

This limited development leads to

$$\varepsilon(1 + 2N\delta^{5/3}) \sim ln(\varphi\,\delta^{-4/3})$$

According to the adsorption condition $N\,\delta^{5/3} \gg 1$, we have then

$$\varepsilon = \frac{1}{2N\delta^{5/3}}ln(\varphi\,\delta^{-4/3}) \tag{38}$$

Replacing ε by its expression (38) in relation (36), we obtain

$$\Gamma(\varphi) \sim \delta^{1/3}\left[1 + \frac{1}{2N\delta^{5/3}}ln(\varphi\,\delta^{-4/3})\right] \tag{39}$$

To calculate the critical volume fraction φ_3, we notice that the term $ln(\varphi/\delta^{-4/3})$ of equation (39) is canceled for bulk concentration $\varphi = \varphi_3 = \delta^{4/3}$.

Then the plateau regime is defined in the interval $\varphi_2 \ll \varphi \ll \varphi_3$ for the volume fraction. The results of all these regimes discussed are presented in Table 1. For the three regimes, the variation of the ratio $(\Gamma(\varphi)/\delta^{1/3})$ according to the ratio $[\varphi/(\delta^{4/3}e^{-N\delta^{5/3}})]$, is given in Fig.5.

Table 1 - The expressions of $\Gamma(\varphi)$ in the different regimes

	Régime (1)	Régime (2)	Régime (3)
	$0 \ll \varphi \ll \varphi_1$	$\varphi_1 \ll \varphi \ll \varphi_2$	$\varphi_2 \ll \varphi \ll \varphi_3$
$\Gamma(\varphi)$		$\frac{1}{2}\delta^{-1}\varphi e^{N\delta^{5/3}}$	$\Gamma \sim \delta^{\frac{1}{3}}\left[1 + \frac{1}{2N\delta^{5/3}}ln(\varphi\delta^{-4/3})\right]$
φ_1	$N^{-\frac{1}{2}}\delta^{\frac{1}{2}}e^{-N\delta^{5/3}}$		
φ_2		$\delta^{4/3}e^{-N\delta^{5/3}}$	
φ_3			$\delta^{4/3}$
φ^*		$\varphi^* \sim N^{-4/5}$	

Regime (1): Diluted in volume and diluted in surface.
Regime (2): Diluted in volume and semi-diluted in surface.
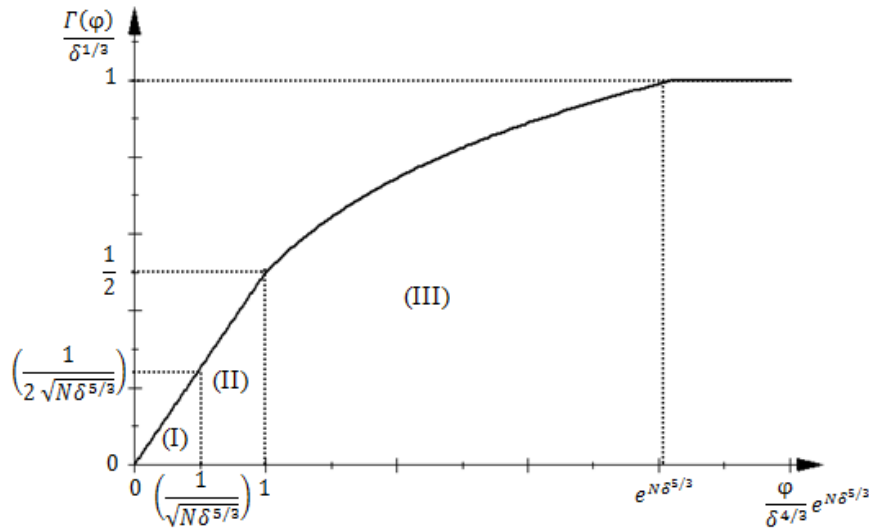Regime (3): Diluted in volume and plateau on the surface.

Fig. 5 - The variation of the ratio $\left(\Gamma(\varphi)/\delta^{1/3}\right)$ depending on the $\left(\varphi/\delta^{\frac{4}{3}}\right)e^{N\delta^{5/3}}$ with (I): regime (1); (II): regime (2); (III): regime (3)

The Figure 5 shows the variation of the surface coverage rate as a function of the volume fraction of monomer. From this figure, we distinguish three regimes:

Regime I: In the case of low volume fraction of monomer, the surface coverage rate increases rapidly when the volume fraction increases, this may be due to the availability of sites for all polymers (PEG) because the surface is not saturated. Consequently, the PEG-chains do not compete to adsorb and have no side interactions when it is adsorbed. In this case the affinity of the polymer for the surface is independent of the coverage rate Γ.

Regime II: The increase in the volume fraction of monomer in the solution makes the surface more and more saturated, and the PEG-chains compete to occupy the available sites. The conformation adopted by the polymers can further change thanks to the repulsive interactions induced (steric) by the monomers of the polymers already adsorbed on the surface.

Regime III: Beyond a critical volume fraction of monomer in solution φ_2, a pseudo-plateau is reached. In this regime, the coverage rate increases very slightly when the volume fraction of monomer φ increases in the solution. This can be explained by the compensation between the attractive forces linked to the affinity of PEG for the natural clay-layer surface and the repulsive forces between the monomers, it becomes impossible, from a physical point of view, for any additional polymer to adsorb.

Forcing the additional adsorption of polymers can be carried out in the case of very high volume fractions of monomer, by increasing the osmotic pressure. These concentrations are difficult to achieve.

2.3 Volume Fraction in Monomer

The adsorption of a polymer on a surface causes a change in the conformation of the chain compared to its conformation in solution [22]. Indeed, for a linear polymer there are three types of substring (Fig. 6), the trains, which are in contact with the surface, the loops, which are not in contact with the surface and which link two trains successive, and the tails, which are the ends of the chain and which are not in contact with the surface. So the absorbed polymer does not form a uniform layer on the surface of the clay sheet, which makes the exact calculation of the thickness of the adsorbed layer difficult, and this is called an average value [23]. In addition, when the affinity of the polymer for the surface is high, the polymer chains are more flattened on the surface, which improves the accuracy of the thickness calculation [24].

To properly describe the conformation of the PEG-chain, we decided to follow the evolution of the concentration along the z axis which is perpendicular to the surface. First put $\varphi(z)$ the number of monomers by the surface D^2 at a distance z from the surface.
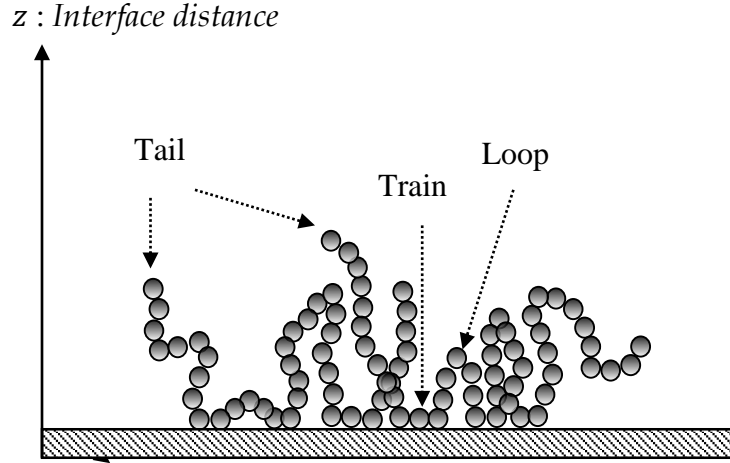
z : Interface distance

Fig. 6 - Conformation of a linear adsorbed polymer [24]

2.3.1 Proximal Zone $a << z << D$

For the proximal zone the volume fraction is given by the formula:

$$\varphi(z) \sim \varphi_s \left(\frac{z}{a}\right)^{-m} \tag{40}$$

with, φ_s represents the fraction in monomer per unit of surface. The goal is to calculate the value of the exponent m by studying the continuity of the equation at $z = D$. For the limit $\delta = \delta_c$ the fraction in monomer per unit of surface is written as: $\varphi_s \sim N^{-3/5}$ for $\delta \ll \delta_c$ and $\varphi_s \sim \delta$ for $\delta \gg \delta_c$

Suppose also that,

$$\int_a^{R_F} \varphi(z)\, dz \sim N^{1-2\nu} \tag{41}$$

Insert equation (40) in the integral (41) we get:

$$\int_a^{R_F} \varphi(z)\, dz \sim \int \varphi_s \left(\frac{z}{a}\right)^{-m} dz$$

$$\int_a^{R_F} \varphi_s \left(\frac{z}{a}\right)^{-m} dz \sim \left[\frac{\varphi_s a^m}{1-m} (R_F)^{1-m}\right]$$

According to (41)

$$\frac{\varphi_s a^m}{1-m} (R_F)^{1-m} \sim N^{1-2\nu}$$

With, $\varphi_s = N^{-3/5}$ in the case where $= \delta_c$, moreover $R_F \sim a\, N^{3/5}$, so that

$$\frac{N^{-3/5} a^m}{1-m} (aN^{3/5})^{1-m} \sim N^{1-2\nu}$$

From the above equation and $\nu = 3/5$, deducing the value of the exponent m is $m = 1/3$. Equation (40) becomes:

$$\frac{\varphi(z)}{\varphi_s} = \left(\frac{z}{a}\right)^{-1/3} \tag{42}$$

2.3.2 Central Zone $D << z << R_F$

For this zone the polymers (PEG) behave like a semi-dilute solution, the value of the volume fraction is given by:

$$\frac{\varphi(z)}{\varphi_s} = \frac{D}{a} \left(\frac{z}{a}\right)^{-4/3} \tag{43}$$

2.3.3 Distal Zone $z >> R_F$

In this zone, there is an exponential fall in the volume fraction [25] [26]:

$$\varphi(z) = cte \; e^{(-z/a)}$$

The volume fraction for $z = R_F$, $\varphi(z = R_F) \sim N^{-4/5}$. Deduce the constant $cte = N^{-4/5}e^{R_F/a}$ then :

$$\frac{\varphi(z)}{\varphi_s} = \frac{D}{a}N^{-4/5} \; e^{(R_F-z)/a} \qquad (44)$$

For the three zones, the variation of the ratio $(\varphi(z)/\varphi_s)$ of the volume fraction $\varphi(z)$ on the fraction of monomer per unit area φ_s as a function of the ratio (z/a) of the direction orthogonal z to the plane of the strong adsorption on the size of the monomer a for the $\gg \delta_c$, is given in Fig.7.
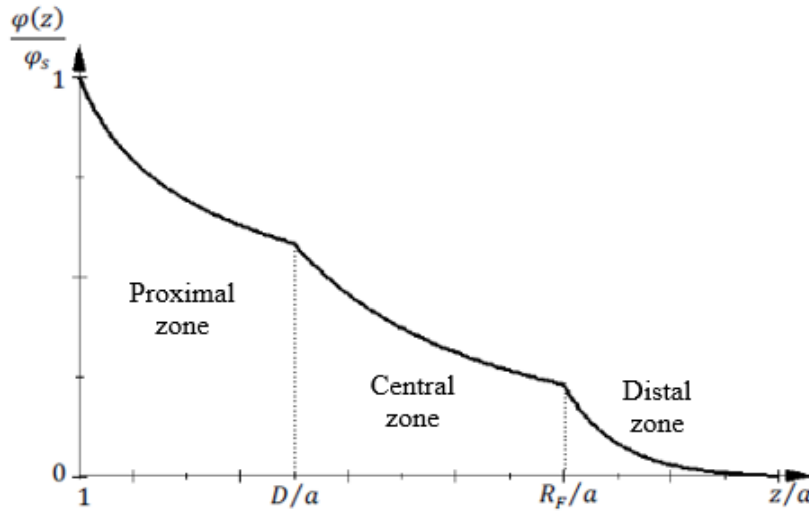

Fig. 7 - Representation of the ratio $(\varphi(z)/\varphi_s)$ as a function of the ratio (z/a), for the three zones in the strong adsorption $\delta \gg \delta_c$
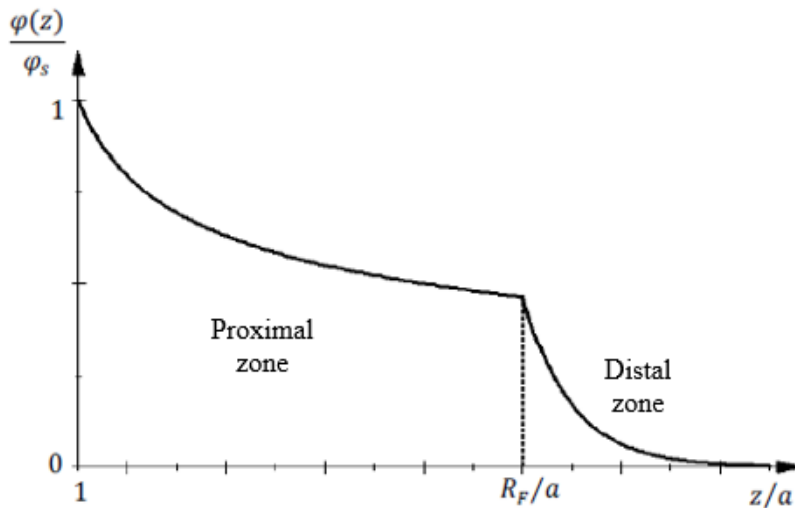

Fig. 8 - Representation of the ratio $(\varphi(z)/\varphi_s)$ as a function of the ratio (z/a), in the weak adsorption $\delta = \delta_c$

For the case where $\delta \ll \delta_c$, we showed the absence of adsorption, but as soon as δ becomes comparable with δ_c (ie $\delta = \delta_c$), we note the appearance of two zones proximal and distal which are presented in Fig.8. The increase in δ reveals a central zone between the two zones with an average volume fraction between that of the proximal zone and the distal zone.

3. Conclusion

In this work, we are interested in the phenomenon of adsorption of flexible PEG-chains from a solution on a natural clay-layer surface assumed to be plane and impenetrable.

In the first part, we discussed the diluted volume regime for which we exposed the three regimes at the level of the adsorption surface. Indeed, when the volume fraction is lower than the critical value φ_1 the surface is diluted and the coverage rate increases rapidly with the increase in the volume fraction, which reflects the strong adsorption of the chains due to the availability of sites at level of the adsorption surface.

We have theoretically shown the continuity of this strong adsorption when the surface changes to the semi-diluted two-dimensional regime, the coverage rate is given by the same equation as that of the diluted regime and increases linearly with the volume fraction of monomer. As soon as the sites available on the surface are mainly occupied, the attraction of the surface with respect to the chains decreases and the rate of coverage of the surface increases logarithmically by the presence of the term $ln(\varphi\delta^{(-4/3)})$ and tends towards saturation, this regime is called plateau regime, the volume is always diluted.

In the second part, we reported the variation of the volume fraction of monomer at the surface level as a function of the orthogonal to the adsorption plane. We have shown that a layer adsorbed on a surface is composed of three zones (proximal, central and distal) with different volume fractions.

The first zone (proximal) is characterized by the contact between the chain and the surface, due to the strong attraction between the two, the volume fraction for this zone which is between a and D, varies as $z^{(-1/3)}$. For the central zone $D < z < R_F$, the volume fraction varies as $z^{(-4/3)}$. Finally, an exponential fall in the volume fraction was noted in the distal area.

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