Acta Montanistica Slovaca Ročník 7 (2002), **4**, 266-270

The role of physico-chemical factors in microbial adhesion
1. Structure and interaction of polyelectrolyte brushes in a good solvent

Jiří Škvarla [1]

Úloha fyzikálno-chemických faktorov v mikrobiálnej adhézii
1. Štruktúra a interakcia polyelektrolytových kief v dobrom rozpúšťadle

Lineárne, flexibilné a elektricky nabité makromolekuly (polyelektrolyty), ktoré sú pútané dostatočne tesne vedľa seba na tuhom povrchu iba jedným koncom (tvoriac tak akúsi „kefu") preukazujú vlastnosti, ktoré sa značne líšia od vlastností obvyklých polymérnych adsorpčných vrtstiev. Tieto špecifické vlastnosti predurčujú polyelektrolytové kefy pre mnohé praktické aplikácie; pretože však zjednodušene pripomínajú povrch biologických objektov, začínajú sa využívať aj pri teoretickom modelovaní štruktúry a interakcie bakteriálnych bunečných stien. Problémom však je stále komplikovanosť a tým praktická nepoužiteľnosť jestvujúcich obecných numerických a analytických riešení. Cieľom práce je preto porovnať známe jednoduché SA (scaling analysis) riešenia (ktoré však neumožňujú stanoviť číselné koeficienty) a exaktnejšie (ale stále jednoduché) riešenia odvodené pre hrúbku vrstvy a repulznú silu medzi dvoma náprotivnými vrstvami v rôznych limitných režimoch. Výsledkom tohto porovnania je zistenie úplnej zhodnosti oboch riešení a určenie príslušných číselných koeficientov. To umožňuje využiť uvedené riešenia SA pri teoretickej interpretácii priamych silových meraní medzi baktériami a povrchmi (experimenty v AFM, Atomic force microscope) a mikrobiálnej adhézie vo všeobecnosti.

Key words: *polyelectrolytes, brushes, structure, disjoining pressure, scaling analysis*

Introduction – polyelectrolyte brushes

The range of the repulsive Coulombic interaction determining the disjoining pressure Π between charged surfaces in polar solvents is determined by the Debye screening length

$$\kappa^{-1} = (4\pi nl)^{-1/2} \qquad 1)$$

i.e. the distance over which the electric fields of these surfaces are screened by a total concentration of monovalent ions n; l is the Bjerrum length – a characteristic lengthscale at which the electrostatic interaction between a pair of monovalent ions has the magnitude of an ambient thermal energy kT. (For pure water at T = 24° C, l = 0.71 nm). We can see that even modest concentrations of salt ions provide a strong screening of the electrostatic repulsion (1 mM electrolyte corresponds to $\kappa^{-1} \approx 10$ nm). However, when charged (ionic) macromolecules are fixed at the surfaces, the Debye screening is less sensitive to the presence of electrolytes because the electrostatic repulsion is combined with the steric interaction due to the entropic polymer elasticity. Unfortunately, a fundamental understanding of the structure and mutual interaction of polyelectrolyte-bearing surfaces in polar solvents still remains to be established. This is partly because bulk polyelectrolyte solutions (unlike solutions of neutral polymers) have eluded any well-unified theoretical picture that would allow the development of a general theory of polyelectrolytes at interfaces.

There are two basic modes of fixation of linear and flexible polymer chains at a surface (de Gennes, 1987; Klein, 1992). If the surface prefers the polymer to the solvent, adsorption of chains is assumed to occur through several segments (junctions), creating a rather loose layer consisting of random trains, loops, and tails (Fig.1a). In the situation where the polymer does not adsorb spontaneously, the chains can be preferentially attached chemically (grafted) to the surface via their ends. In good solvent conditions, the chains repel each other and the grafting reaction terminates when they are disposed as adjacent „mushrooms" (Fig.1b). In favourable cases, the density of grafting points is higher, providing a thick „brush" layer with a rather constant concentration of segments (Fig.1c). The end grafting may be achieved by covalently bonding the polymer to the surface with a chemically active end group or by anchoring a copolymer („macrosurfactant") by a (possibly nonpolar) block, with a polyelectrolyte as the other block.

A detailed analysis of the intrinsic structure and interaction of the polyelectrolyte brush was performed by Borisov et al. (1994), Lyatskaya et al. (1995), Zhulina and Borisov (1997), and Tamashiro et al. (2001) on the basis of the self-consistent-field theory. However, the SCF results are too complicated as a rule. On the other hand, although the scaling analysis, beneficiating from the self-similarity feature of the polymer layers, is not precise (it does not predict the numerical coefficients in any formula), it does provide a satisfactory insight.

Presently, we are faced with a series of publications on the direct measurements of interactions between real polyelectrolyte brushes [see e.g. Abraham et al., 2000; Kelley et al., 1998; Prinz et al., 2000; Tran et al.

---

[1] *Doc. Ing. Jiří Škvarla, CSc.*, Department of Mineral Processing and Environmental Technologies Technical University of Košice, Park Komenského 19, 04384 Košice, Slovak Republic. Fax: 421-55-6022957; e-mail: Jiri.Skvarla@tuke.sk
(Recevied 20.6.2002)

(1999)] as well as between bacteria and solid surfaces using the AFM technique (Atomic Force Microscopy), revealing a polyelectrolyte character of the bacterial cell wall (see e.g. Beech et al., 2002; Camesano and Logan, 2000; Considine et al., 2001; Frank and Belfort, 1997; Razatos et al., 1998; etc.). Consequently, the polyelectrolyte brushes, resembling the bacterial cell wall architecture, have been adopted to model microbial adhesion.

The aim of this paper is to compare available results of scaling analysis and a more exact solution of the structure and interaction (disjoining pressure) of polyelectrolyte brushes.

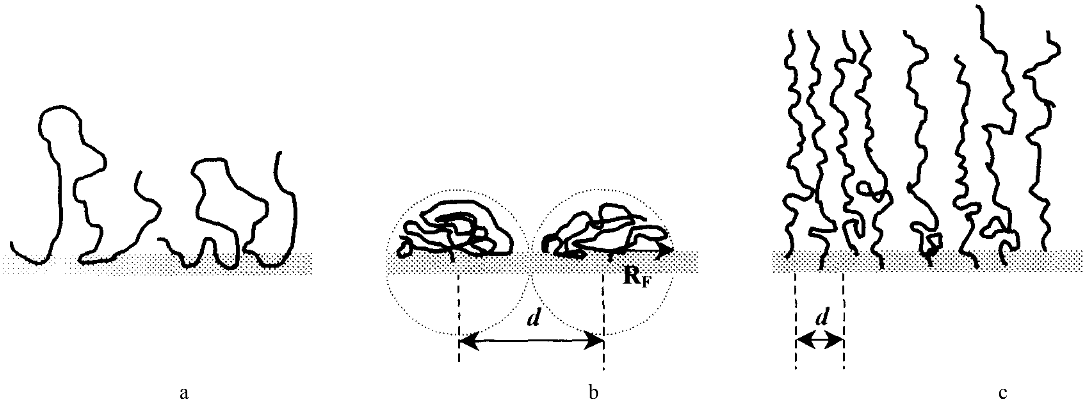

Fig.1 Modes of fixation of macromolecular chains on a surface: adsorption through random segments (a), end-grafting of a low density – the distance between grafting points d is larger than the coil size R_F („mushrooms“ mode) (b), end-grafting of a high density with d < R_F („brushes“ mode) (c).

Obr.1 Spôsoby pútania makromolekulárnych reťazcov na povrch: adsorpcia náhodnými segmentami (a), koncové spojenia s nízkou hustotou – vzdialenosť medzi spojovacími bodmi d je väčšia ako rozmer klbka R_F („huby“) (b), koncové-spojenia s vysokou hustotou a d < R_F („kefy“) (c)

Scaling analysis results

In the pioneering publication of Pincus (1991), simple analytical scaling laws for structural and interaction parameters such as the thickness, counterion distribution and disjoining pressure of opposing layers of monodisperse polyelectrolyte end-grafted to a flat solid surface in contact with a polar (good) solvent (polyelectrolyte brush) was provided, approximating the results of numerical solutions of the electrostatic mean-field equations (Poisson-Boltzmann equation) coupled to elasticity of the polyelectrolyte brush by Misra et al. (1989) and Miklavic and Marčelja (1988). An uniform or „flat“ distribution of monomers throughout the brush region – a step function concentration profile was considered. Different regimes corresponding to different counterion distributions have been defined.

1. Considering counterions as a constrained ideal gas, the disjoining pressure Π between two identical *charged surfaces without polyelectrolytes* separated by a distance 2*h* (the dominant effect of electrostatics is to preserve local charge neutrality at the expense of the mixing entropy of counterions which is increased if they can explore a larger volume) is:

$$\Pi \cong kT/2\pi l h^2 \qquad h >> \lambda \tag{2a}$$

$$\Pi \cong kT/\Sigma h \qquad h < \lambda \tag{2b}$$

where the Bjerrum length is $l = e^2/4\pi\varepsilon kT$ (*e* is the electronic charge and ε is the dielectric constant of the solvent) and $\lambda = \Sigma/2\pi l$ is the Gouy-Chapman length (Σ^{-1} is the surface charge density), i.e. the distance from the charged surface in which the ions are localized (the Debye screening length associated with the mean counterion density).

2. The disjoining pressure between two identical *brushes of end-grafted neutral polymers* in a good solvent is determined by balancing the excluded-volume repulsion tending to swell the chains (in the mean-field theory, the osmotic pressure corresponding to a local monomer concentration *c* is $P = ½\nu^2 ckT$ against the entropic (Gaussian) polymer elasticity ($P = kL/d^2$, where the elastic constant *k* for a random walk chain is $k \cong kT(Na^2)^{-1}$):

$$\Pi = (1/2)\nu c^2 kT \approx \nu N^2 kT h^2/d^4 \tag{3}$$

where ν is the excluded volume per monomer, $c = N/d^2 h$ is the local monomer concentration in the semidilute or denser range, *N* is the degree of polymerization, and *d* is the (fixed) mean grafting spacing of the polyelectrolyte. At the equilibrium condition, the thickness of the brush is:

$$L = Na\left(\frac{\nu}{2ad^2}\right)^{1/3} \tag{4}$$

urthermore, two possible regimes have been distinguished by using the simple force balance approach for polyelectrolyte brushes defining a distance scale over which a test charge is neutralized ξ (neutralization length) and ignoring the repulsive excluded-volume effect: $L \geq \xi$ (strong charging) and $L \leq \xi$ (weak charging).

3. *Strong charging, no electrolyte („osmotic regime").* At $L \geq \xi$ the brush thickness is determined by a balance between the swelling effect of the counterion entropy and the chain elasticity. In this regime the role of the electrostatics is to establish the neutralization length but it is not explicitly involved in determining the global brush thickness because the neutrality is only local. Thus, L may be found in a similar manner to the derivation of Eq.4, using $P = kL/d^2$ where now $P = fckT$ is the counterion osmotic pressure and the monomer concentration is $c = N/d^2L$ (the local neutrality condition is used to identify the counter ion concentration with c):

$$L \cong Naf^{1/2} \tag{5}$$

and the neutralization length is then given by the Debye screening length with the counterion concentration fc:

$$\xi \cong d(a/4\pi lf^{1/2})^{1/2} \tag{6a}$$

Thus, the condition $L \geq \xi$ applies unless $Nf^{3/4} \leq d(4\pi la)^{1/2}$. The above result for L is valid for strongly charged polymers and high grafting densities (the chains are highly stretched for finite charging) and is independent of the grafting density.

Two domains have been delimited:

a. *Large separations $h \geq L$.* The system behaves as highly charged interfaces and Π is given by (compare with Eq.2b):

$$\Pi = kT/2\pi lh^2 \tag{7a}$$

b. *Compressed brushes $h \leq L$.* Π is given by the counterion osmotic pressure $P = fckT$ ($c = N/d^2h$)

$$\Pi \cong fNkT/d^2h \tag*{7b)}$$

The latter result exceeds that for neutral brushes (Eq.3) at same d and N ($v/d^2h \leq 1$ and $N/f \geq 1$). When the compressed brushes start to overlap, i.e. $h \approx L$, there is a jump (sharp increase) in $\Delta\Pi \cong f^{1/2}kT/d^2a$ occuring over the screening length ξ due to the elastic energy stored in the stretched chains.

4. *Weak charging, no electrolyte (Pincus regime).* If $L << \xi$ the counterion distribution extends beyond the brush due to the insufficient electrostatic attraction between the anchored polyions and the mobile counterions. Then, as viewed from a far, the brush resembles a simple charged surface of charge density fN/d^2. The length ξ is given by the Gouy-Chapman length λ:

$$\xi \cong \frac{d^2}{2\pi lNf} \tag{6b}$$

The counterion swelling pressure on the polymers is reduced by the fraction remaining within the brush region L/ξ.. The force balance is then given:

$$P \cong fc(L/\xi)kT \cong kL/d^2 \tag{8}$$

and

$$L \cong 2\pi lN^3(fa/d)^2 \tag{9}$$

which crosses to Eq.5 when $\xi = L$. Again, there are two regimes delimited by h/ξ :

$$\Pi \cong kT\left(2\pi lh^2\right)^{-1} \qquad h > \xi \tag{10}$$

Eq.7b $\qquad h < \xi$

(it is important to note that Π here are numerically much weaker than Π in the strong charge regime).

5. *Added electrolyte, weak screening (f = 1).* The added electrolyte influences the brush structure only when its concentration c_s is sufficiently large that the corresponding Debye screening length κ_s^{-1} is comparable to the neutralization length ξ. When $\kappa_s^{-1} >> \xi$ (weak screening limit) the only effect of the electrolyte is in the outer fringes ($x \geq L$) of the brush where the counterion concentration becomes equivalent to that of salt. Then for $\kappa_s h \geq 1$ the disjoining pressure decays exponentially:

$$\Pi \cong kT\,(\kappa^2/2\pi l)\mathrm{e}^{-\kappa h} \tag{11}$$

This crosses over to the standard charged surface result in the range $L \leq h \leq \kappa_s^{-1}$.

6. *Added electrolyte, strong screening (f = 1).* As the salt concentration increases so as $\kappa_s\xi \geq 1$, the Debye screening starts to reduce the counterion osmotic pressure (which stretches the polymers). The osmotic pressure of a semidilute polyelectrolyte solution in the presence of salt is

$$P \cong ckT(\kappa_0/\kappa)^2 \tag{12}$$

where κ_0 is the Debye length associated with the counterions alone and $\kappa^2 \equiv \kappa_0^2 + \kappa_s^2$. Thus, in the limit $\kappa_0^{-1} >> \kappa_s^{-1}$, $P \cong c^2kT/2c_s$ (note the crossover from linear to quadratic dependence on the monomer concentration when salt is added) and we can again balance the osmotic pressure (Eq.12) against the polymer entropy loss on expanding

$$P \cong LkT\left[N(ad)^2\right]^{-1} \tag{13}$$

which in the strong screening limit gives

$$L \cong Na\left(2ad^2 c_{\mathrm{s}}\right)^{-1/3} \tag{14}$$

and there is an intermediate strong screening regime of disjoining pressure:

$$\Pi \cong (1/2)(kT/c_{\mathrm{s}})\left(N/d^2 h\right)^2 \tag{15}$$

which is valid for $L \geq h \geq h^*$. When $h < h^* \cong N(2d^2 c_{\mathrm{s}})^{-1}$ the counterion distribution is sufficiently compressed that its concentration exceeds $2c_{\mathrm{s}}$ and the disjoining pressure crosses over into the regime described by Eq.7b. Thus, the central result of the Pincus work was that in the strong screening regime, a power law dependence of the disjoining pressure on interplanar spacing is maintained with a crossover from h^{-1} at small separations to h^{-2} at larger separations (with a final drop to small values at $h \approx L$), confirming the validity of the assumption about the suppressed Debye screening effect in polyelectrolyte brushes owing to their elasticity.

Box model results

Wittmer and Joanny (1993) rederived the Pincus scaling results considering a diblock copolymer (where one of the blocks is a charged polyelectrolyte) adsorbed from its micellar solution at an interface. An extremely simplified description of the electrostatics – the box model was used, ignoring the detailed variation of the monomers and counterions concentrations and replacing them with constants over certain regions. All their results are identical to those obtained by Pincus within numerical prefactors of order unity. So (see also Tran et al., 1999) for the strong charging limit they arrived at

$$L = 3^{-1/2} Naf^{1/2} \tag{16}$$

which is Eq.5 with a prefactor $3^{-1/2}$. Similarly, for the weak charging they received:

$$L = (4\pi/9) lN^3 (fa/d)^2 \tag{17}$$

which is exactly Eq.9 with a prefactor 2/9. But for the strong screening limit, the following scaling formula was derived:

$$L \cong Naf^{2/3}(2ad^2 c_{\mathrm{s}})^{-1/3} \tag{18}$$

which is the scaling Eq.14 (derived for $f = 1$) with added $f^{2/3}$.

Exact results

Ohshima (1999) calculated the repulsive electrostatic force per unit area (disjoining pressure) between two neutral plates covered with an uniform charged polymer brush layer of intact thickness d_0 (immersed in a symmetrical electrolyte and penetrable to the electrolyte ions as well as water molecules) as a function of their separation distance h:

$$\Pi = 64nkT \tanh(y_0/4)\exp[-\kappa(h-2d_0)] \qquad \text{(intact brushes, } h \geq 2d_0\text{)} \tag{19}$$

$$\Pi = 2nkT\left[\sqrt{1+\left(\frac{zN_0 d_0}{\upsilon nh}\right)^2}-1\right] \qquad \text{(compressed brushes, , } h \leq 2d_0\text{)} \tag{20}$$

where n and υ are the bulk concentration and valence of the electrolyte, N_0 and z is the number density and valence of the dissociated groups, κ is the Debye-Hückel parameter $(2\upsilon^2 e^2 n/\varepsilon_{\mathrm{r}}\varepsilon_0 kT)^{1/2}$ and y_0 is the scaled unperturbed potential at the front edge of the intact brush layer and the surrounding electrolyte solution (before the two brushes come into contact).

Eq.20, developed for the compressed brushes which come into contact, squezze against each other but do not interdigitate, provides the following limits for highly charged brushes, independent of the electrolyte concentration n:

$$\Pi = \frac{2|z|N_0 d_0 kT}{\upsilon h} \qquad \left|\frac{zN_0}{\upsilon n}\right| >> 1 \tag{21a}$$

and for weakly charged brushes:

$$\Pi = \frac{(zN_0 d_0)^2 kT}{\upsilon^2 nh^2} \qquad \left|\frac{zN_0}{\upsilon n}\right| << 1 \tag{21b}$$

It is now clear that $N_0 \equiv fN/d^2d_0$ so that Eq.21a (valid for strong charging) can be rewritten as:

$$\Pi = \frac{2|z|fNkT}{d^2 \upsilon h} \tag{22a}$$

Eq.22a is equal to Eq.7b with a prefactor $|z|/\upsilon$. (Remember that Ohshima considers the separation distance h instead of $2h$ assumed by Pincus). Similarly, Eq.21b (valid for strong screening) can be rewritten as

$$\Pi = \frac{(zfN)^2 kT}{d^4 \upsilon^2 n h^2} \tag{22b}$$

which is equal to Eq.15 with a prefactor z^2/υ^2.

References

ABRAHAM, T., GIASSON, S., GOHY, J.F., and JÉRÔME, R.: Direct measurements of interactions between hydrophobically anchored strongly charged polyelectrolyte brushes. *Langmuir*, 16, 2000, p. 4286-4292.

BEECH, I.B., SMITH, J.R., STEELE, A.A., PENEGAR, I., and CAMPBELL, S.A.: The use of atomic force microscopy for studying interactions of bacterial biofilms with surfaces. *Colloids Surfaces*, 23, 2002, p. 231-247.

BORISOV, O.V., ZHULINA, E.B., and BIRSHTEIN, T.M.: Diagram of the states of a grafted polyelectrolyte layer. *Macromolecules*, 27, 1994, p. 4795-4803.

CAMESANO, T.A. and BRUCE, E.L.: Probing bacterial electrosteric interactions using atomic force microscopy. *Environ. Sci. Technol.*, 34, 2000, p. 3354-3362.

CONSIDINE, R.F., DRUMMOND, C.J., and DIXON, D.R.: Force of interaction between a biocolloid and an inorganic oxide: complexity of surface deformation, roughness, and brushlike behavior. *Langmuir*, 17, 2001, p. 6325-6335.

De GENNES, P.G.: Polymers at an interface; a simplified view. *Advan. Colloid Inter. Sci.*, 27, 1987, p. 189-209.

FRANK, B.P. and BELFORT, G.: Intermolecular forces between extracellular polysaccharides measured using the atomic force microscope. *Langmuir*, 13, 1997, p. 6234-6240.

GRANTHAM, M.C. and DOVE, P.M.: Investigation of bacterial-mineral interactions using fluid tapping mode atomic force microscopy. Geochim. *Cosmoch. Acta*, 60, 1996, p. 2473-2480.

KELLEY, T.W., SCHORR, P.A., JOHNSON, K.D., TIRRELL, M., and FRISBIE, C.D.: Direct force measurements at polymer brush surfaces by atomic force microscopy. *Macromolecules*, 31, 1998, p. 4297-4300.

KLEIN, J.: Long-ranged surface forces: the structure and dynamics of polymers at interfaces. *Pure Appl. Chem.*, 64, 1992, p. 1577-1584.

LYATSKAYA, Yu.V., LEERMAKERS, F.A.M., FLEER, G.J., ZHULINA, E.B., and BIRSHTEIN, T.M.: Analytical self-consistent-field model of weak polyacid brushes. *Macromolecules*, 28, 1995, p. 3562-3569.

MIKLAVIC, S.J. and MARČELJA, S.: Interaction of surfaces carrying grafted polyelectrolytes, *J. Phys. Chem.*, 92, 1988, p. 6718-6722.

MISRA, M., VARANASI, S., and VARANASI, P.P: A polyelectrolyte brush theory. *Macromolecules*, 22, 1989, 4173-4179.

OHSHIMA, H.: Electrostatic repulsion between two parallel plates covered with polymer brush layers. *Colloid Polymer Sci.*, 277, 1999, p. 535-540.

PINCUS, P.: Colloid stabilization with grafted polyelectrolytes. *Macromolecules*, 24, 1991, p. 2912-2919.

PRINZ, C., MULLER, P., and MALOUM, M.: Annealed polyelectrolyte brushes under normal and lateral compressions. *Macromolecules*, 33, 2000, p. 4896-4902.

RAZATOS, A., ONG, Y-L., SHARMA, M.M., and GEORGIOU, G.: Evaluating the interaction of bacteria with biomaterials using atomic force microscopy. *J. Biomater. Sci. Polymer Edn.*, 9, 1998, p. 1361-1373.

TAMASHIRO, M.N., HERNÁNDEZ-ZAPATA, E., SCHORR, P.A., BALASTRE, M., TIRRELL, M., and PINCUS, P.: Salt dependence of compression normal forces of quenched polyelectrolyte brushes. *J. Chem Phys.*, 115, 2001, p.1960-1964.

TRAN, Y., AUROY, P., and LEE, L-T.: Determination of the structure of polyelectrolyte brushes. *Macromolecules*, 32, 1999, p. 8952-8964.

WITTMER, J. and JOANNY, J.F.: Charged diblock copolymers at interfaces. *Macromolecules*, 26, 1993, p. 2691-2697.

ZHULINA, E.B., BORISOV, O.V., and BIRSHTEIN, T.M.: Structure of grafted polyeletrolyte layer. *J. Phys. II. France*, 2, 1992, p. 63-74.

ZHULINA, E.B. and BORISOV, O.V.: Structure and interaction of weakly charged polyelectrolyte brushes: Self-consistent field theory. *J. Chem. Phys.*, 107, 1997, p. 5952-5967.