Electrophoretic mobility of soft particles. A soft step function model

Hiroyuki Ohshima [a],[b],[*]

[a] *Faculty of Pharmaceutical Sciences, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan*
[b] *Center for Colloid and Interface Science, Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan*

HIGHLIGHTS

- We model the inhomogeneous distribution of polymer segments by a soft step function.
- We derive an approximate analytic expression for the electrophoretic mobility of a soft particle.
- The mobility of a soft particle decreases by the inhomogeneous segment distribution.

GRAPHICAL ABSTRACT
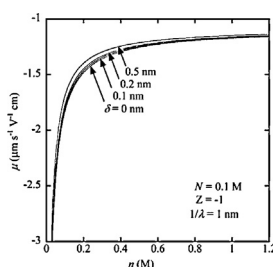
ARTICLE INFO

ABSTRACT

A simple approximate analytic expression is derived for the electrophoretic mobility of a soft particle consisting of the hard particle core covered with an ion-penetrable surface layer of polyelectrolytes. The effect of the inhomogeneous distribution of the polymer segments is taken into account by modeling the surface layer as a soft step function with the inhomogeneous distribution width δ. The mobility expression, which is derived on the basis of the non-linear Poisson–Boltzmann equation, improves an approximate mobility expression previously derived by using the linearized Poisson–Boltzmann equation.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The electrophoretic mobility of polyelectrolyte-coated particles, which we term soft particles, has been studied theoretically by a number of researchers [1–28]. These studies are based on the Debye–Bueche model [29] in which the polymer segments are regarded as resistance centers distributed uniformly in the polyelectrolyte layer, exerting frictional forces on the liquid flowing in the polyelectrolyte layer.

The polyelectrolyte layer is usually modeled as a hard step function, that is, the surface charge layer assumed to have a definite thickness with a uniform segment density distribution. The hard step function model is an idealized model. A more realistic model is the one that takes into account the effect of the inhomogeneous distribution of polymer segments. Indeed, there are some cases in which this effect becomes important. Varoqui [30] and Ohshima [31] considered the case where neutral polymers are adsorbed with an exponential segment density distribution. Duval and Ohshima [32] have presented an electrokinetic theory of diffuse soft particles by modeling the polyelectrolyte layer as a sigmoidal function.

Recently, as a different model we have proposed a soft step function model [33]. This theory, however, is based on the linearized Poisson–Boltzmann equation and thus is applicable only for the low

* Corresponding author at: Faculty of Pharmaceutical Sciences, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan.
Tel.: +81 4 7124 1501x6772; fax: +81 04 7121 4483.
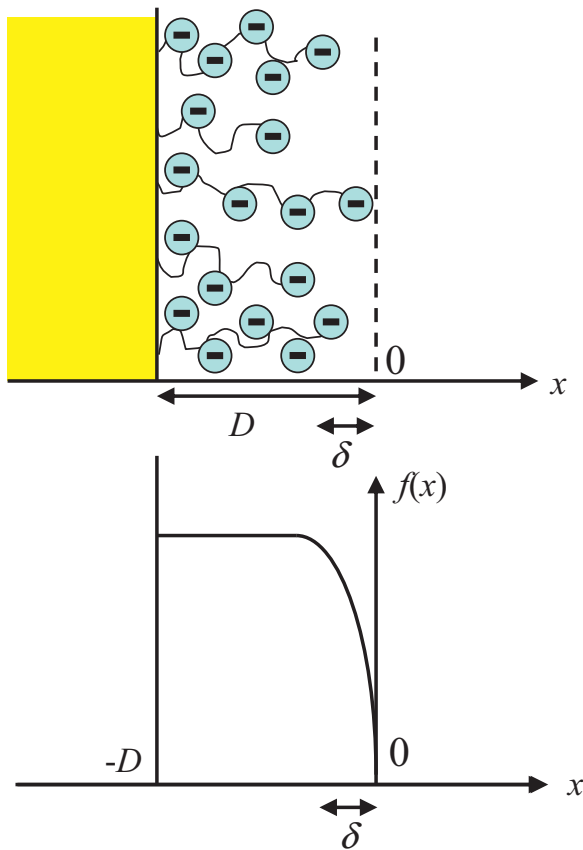*E-mail addresses:* ohshima@rs.noda.tus.ac.jp, ohshima@rs.noda.tus.ac.jp

Fig. 1. Schematic representation of the surface of a plate-like particle covered by an ion-penetrable surface layer of polyelectrolytes (upper) and the segment density distribution modeled as a soft step function with the inhomogeneous segment distribution width δ (lower).

potential case. In the present paper we will improve the previous result by using the non-linear Poisson–Boltzmann equation.

2. Potential distribution

Consider a soft particle immersed in a symmetrical electrolyte solution of valence z and bulk concentration (number density) n. The particle consists of an uncharged core covered with an ion-penetrable surface layer of polyelectrolytes of thickness D. We treat the case where the particle size is much larger than the Debye length $1/\kappa$ so that the particle surface can be assumed to be planar. Here κ is the Debye–Hückel parameter, defined by

$$\kappa = \left(\frac{2z^2e^2n}{\varepsilon_r\varepsilon_o kT} \right)^{1/2} \tag{1}$$

where e is the elementary electric charge, ε_r is the relative permittivity of the electrolyte solution, ε_o is the permittivity of a vacuum, k is Boltzmann's constant, and T is the absolute temperature.

We take an x-axis perpendicular to the particle surface with its origin 0 at the front edge of the surface charge layer so that the region $x > 0$ corresponds to the solution phase (Fig. 1). We assume that the polymer segment distribution can be modeled as a soft step function so that its distribution function $f(x)$ is given by

$$f(x) = 1 - \exp\left(\frac{x}{\delta}\right), \quad -D < x < 0 \tag{2}$$

Here δ, which is assumed to satisfy $\delta \ll D$, is a measure of the width of the inhomogeneous distribution of polyelectrolyte segments

near the front edge of the polyelectrolyte layer. Eq. (2) implies that D corresponds to the maximum segment length.

We assume that ionized groups of valence Z are distributed in the polyelectrolyte layer and their density $N(x)$, which is a function of x, is proportional to the distribution function $f(x)$. We also assume that D is much thicker than δ ($\delta \ll D$) so that the density $N(x)$ can be assumed to have a constant value N in the deep inside the surface layer. We may thus write

$$N(x) = Nf(x) = N\left\{1 - \exp\left(\frac{x}{\delta}\right)\right\}, \quad -D < x < 0 \tag{3}$$

The surface charge density $\rho_{\text{fix}}(x)$ is thus given by

$$\rho_{\text{fix}}(x) = ZeN(x) = ZeNf(x) = ZeN\left\{1 - \exp\left(\frac{x}{\delta}\right)\right\}, \quad -D < x < 0 \tag{4}$$

We assume that the electric potential $\psi(x)$ at position x satisfy the following nonlinear Poisson–Boltzmann equations:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_{\text{el}}(x) + \rho_{\text{fix}}(x)}{\varepsilon_r\varepsilon_o}, \quad -D < x < 0 \tag{5}$$

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_{\text{el}}(x)}{\varepsilon_r\varepsilon_o}, x > 0 \tag{6}$$

with

$$\rho_{\text{el}}(x) = ZeN(e^{-y} - e^y) \tag{7}$$

where

$$y(x) \equiv \frac{ze\psi(x)}{kT} \tag{8}$$

is the scaled electric potential. Eq. (5) implies that the relative permittivity ε_r takes the same value both inside and outside the surface charge layer.

By using Eqs. (4), (7) and (8), the Poisson–Boltzmann Eqs. (5) and (6) become

$$\frac{d^2y}{dx^2} = \kappa^2\{\sinh y - \sinh y_{\text{DON}}(1 - e^{x/\delta})\}, \quad -D < x < 0 \tag{9}$$

$$\frac{d^2y}{dx^2} = \kappa^2 \sinh y, \quad x > 0 \tag{10}$$

with

$$y_{\text{DON}} \equiv \frac{zey_{\text{DON}}}{kT} = \text{arcsinh}\left(\frac{ZN}{2zn}\right) = \ln\left[\frac{ZN}{2zn} + \sqrt{\left(\frac{ZN}{2zn}\right)^2 + 1}\right] \tag{11}$$

where ψ_{DON} is the Donnan potential and y_{DON} is the scaled Donnan potential. As a good approximation, we put $y = y_{\text{DON}} + \Delta y$ in Eq. (9) and linearize Eq. (9) with respect to Δy, giving

$$\frac{d^2\Delta y}{dx^2} = \kappa_m^2\Delta y + \kappa_m^2 \tanh y_{\text{DON}}e^{x/\delta} \tag{12}$$

with

$$\kappa_m = \kappa\sqrt{\cosh y_{\text{DON}}} = \kappa\left[1 + \left(\frac{ZN}{2zn}\right)^2\right]^{1/4} \tag{13}$$

where κ_m can be interpreted as the Debye–Hückel parameter inside the surface layer. The boundary conditions are

$$\left.\frac{dy}{dx}\right|_{x=-D} = 0 \tag{14}$$

$$\left.\frac{dy}{dx}\right|_{x=0^-} = \left.\frac{dy}{dx}\right|_{x=0^+} \tag{15}$$