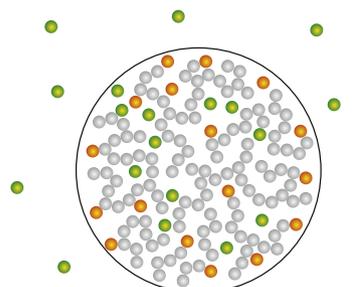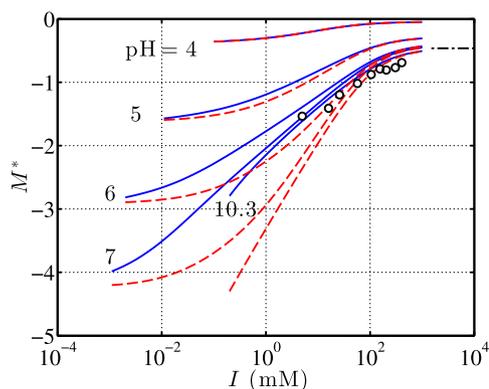# On the electrophoretic mobility of succinoglycan modelled as a spherical polyelectrolyte: From Hermans-Fujita theory to charge regulation in multi-component electrolytes

CrossMark

Reghan J. Hill

Department of Chemical Engineering, McGill University, Montreal, Quebec H3A OC5, Canada

GRAPHICAL ABSTRACT

ABSTRACT

Literature interpretations of the electrophoretic mobility of spherical polyelectrolytes are revisited using the capillary-electrophoresis data of Duval et al. (2006) for the extracellular polysaccharide succinoglycan as an example. Subtle changes in the polyelectrolyte mobility have recently been attributed to new electrokinetic theories that feature multi-component electrolytes, charge regulation, and the so-called polarization and relaxation phenomena. However, these calculations exhibit several unusual trends that have yet to be explained, and so the conclusions drawn from them are controversial. Here, independent computations strengthen conclusions drawn from the original model of Duval et al., i.e., the discrepancies between experiments and all the presently available electrokinetic theories reflect changes in the conformation of succinoglycan arising from changes in the electrolyte pH and ionic strength.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

This study addresses subtle features of the electrophoretic mobility versus ionic-strength relationship for succinoglycan macromolecules. Duval et al. [2] measured this relationship and

interpreted the data using electrokinetic models for spherical and rod-like polyelectrolytes, explicitly addressing changes in the charge arising from changes in the pH and ionic strength of the electrolyte, hereafter termed charge regulation. Their model furnished estimates of the protolytic binding site density and equilibrium dissociation constants. Moreover, the theory advanced the well-known Hermans-Fujita model to account for non-linear elec-

E-mail address: reghan.hill@mcgill.ca

trostatics (via the non-linear Poisson–Boltzmann equation), ion-concentration perturbations—also termed double-layer-polarization (DLP)—and charge regulation.

However, two recent theoretical studies by Yeh and coworkers [11,10] (both using finite-element (FE) modelling software to compare models with an without DLP) argued that new electrokinetic models elucidate the subtle changes in the mobility-ionic-strength relationship (elaborated upon below) not captured by the model of Duval et al. [2] Both Yeh and coworkers' theoretical interpretations predict that DLP increases the magnitude of the mobility at high ionic strengths, as evidenced by a crossing of the mobility versus ionic strength relationships undertaken with and without DLP. As discussed in the SI, this unusual behaviour is contrary to the general expectation that DLP decreases the mobility magnitude. Moreover, the charge-regulation model of Yeh et al. [11] is not fundamentally different from the model of Duval et al. [2], since both include charge regulation closures, and both account for DLP (the latter attribute seems to have been overlooked by Yeh and coworkers).

Attributing the qualitative differences between the theoretical calculations to new physics is controversial, and surely demands further investigation. The anomalies in question might be considered minor and, therefore, inconsequential from a practical perspective. However, such nuances have been used to highlight new physical insights and to motivate intricate mathematical models for interpreting experiments, e.g., as tools for parameter fitting. Knowledge of whether differences between model predictions can be attributed to new physics or, perhaps, computational artifacts is clearly important.

The challenges of accurately solving particle-electrophoresis models are well known [8]. Indeed, these motivate analytical approximate theories, such as the Hermans-Fujita formula, and specialized computational methods, as implemented below. The solution methodology adopted in this study will be demonstrated to agree with the calculations of Duval et al. [2] (Fig. 1) and the Hermans-Fujita theory (Fig. 2). While the former tests general aspects of the electrokinetic model, including charge regulation, non-linear electrostatics, and DLP, the latter tests computational fidelity under the most challenging conditions where disparities in particle and diffuse-layer length scales are very large ($\kappa a \gg 1$).
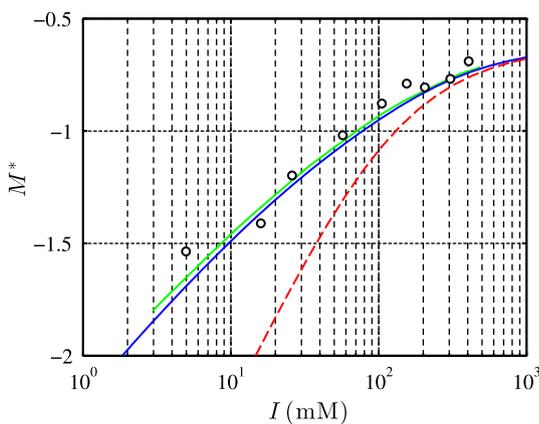

Fig. 1. Electrophoretic mobility compared with Duval et al. [2] (charge regulation, nonlinear electrostatics, DLP): $a = 10.8$ nm, $\ell = 0.7$ nm, $n_{f,1,0}^* = 0.239$ M, $pK_1 = 4.58$ and $pK_2 = 8.60$ at pH = 10.3. The green line is the data labelled as 'rigorous theory' from Fig. 3B of Duval et al. [2], which they evaluated using the computational methodology of Duval and Ohshima [1]; the blue solid (red dashed) lines are calculations using the same charge-regulating electrokinetic model of Duval et al. [2] (two acid-dissociation moieties) evaluated with (without) DLP. Symbols are the experimental data of Duval et al. [2]. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)
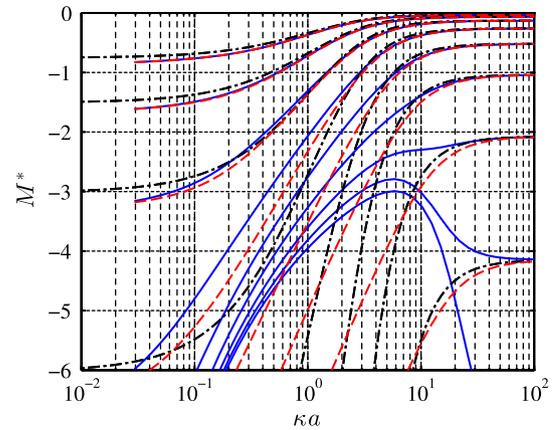

Fig. 2. Spherical polyelectrolyte electrophoretic mobility versus scaled reciprocal Debye length κa : $a = 20$ nm, $\ell = 2$ nm, and fixed charge densities $\rho_f = 1, 2, 4, \ldots, 128, 256$ mM (top to bottom). The blue solid (dashed red) lines are calculations ($\delta = L/100$ with electrolytes containing H$^+$, Cl$^-$, Na$^+$ and OH$^-$ ions at pH = 7) with (without) DLP. The black dash-dotted lines are Eq. (4) (Hermans-Fujita theory: Debye-Hückel approximation without DLP). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

2. Electrokinetic model

The calculations reported here were undertaken using the same methodology that underlies the MPEK package, which emerged from early attempts to capture the electrostatic non-linearities and polarization and relaxation dynamics for soft colloidal spheres with an impenetrable core and a soft, possibly charged, permeable corona [7,6]. Here, it was modified to include proton-donating and proton-accepting sites. Accordingly, for the zwitterionic regulation model of Yeh and coworkers, the immobile charge density ρ_f arising from the groups X$_1$H (acid, –COOH) and X$_2$ (base, –NH$_2$) associated with H$^+$ was prescribed according to equilibria
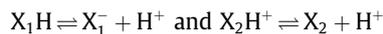
$$X_1H \rightleftharpoons X_1^- + H^+ \text{ and } X_2H^+ \rightleftharpoons X_2 + H^+$$

with equilibrium constants $K_1 = [X_1^-][H^+]/[X_1H]$ and $K_2 = [X_2][H^+]/[X_2H^+]$, and binding-site densities $n_{f,1}^* = [X_1H] + [X_1^-]$ and $n_{f,2}^* = [X_2H^+] + [X_2]$. It follows that

$$[X_1^-] = \frac{n_{f,1}^*}{1 + [H^+]/K_1} \text{ and } [X_2H^+] = \frac{n_{f,2}^*}{1 + K_2/[H^+]},$$

so the immobile charge density for this charge-regulation model can be written

$$\rho_f = -\frac{en_{f,1}^*}{1 + [H^+]/K_1} + \frac{en_{f,2}^*}{1 + K_2/[H^+]}.$$

Details of the electrokinetic model, which addresses a much more general class of charge-regulating spherical nanoparticulates comprising a rigid, impenetrable core and a porous corona, are available elsewhere [4]. To model a porous sphere, the radius of the nanoparticle core a_c must be set to a value that is much smaller than the nominal thickness L of the corona. In this limit, the charge and hydrodynamic drag of the vanishingly small core become negligible to the charge and drag on the corona. In this study, a porous sphere is prescribed using a Stokes-segment density profile

$$n_s(r) = n_{s,0} 0.5 \text{erfc}[-(r - L - a_c)/\delta] \quad (1)$$

and accompanying radial binding-site profiles

$$n_{f,1}^*(r) = n_{f,1,0}^* 0.5 \text{erfc}[-(r - L - a_c)/\delta] \quad (2)$$

$$n_{f,2}^*(r) = n_{f,2,0}^* 0.5 \text{erfc}[-(r - L - a_c)/\delta]. \quad (3)$$