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Electrokinetic potential of polystyrene particles in polyelectrolyte and polyelectrolyte mixtures solutions

Sandor Barany^{a,*}, Martin Nagy^b, Jiri Skvarla^b

^a University of Miskolc, Institute of Chemistry, 3515 Miskolc-Egyetemvaros, Hungary ^b Technical University of Kosice, Kosice, Letna ul. 9, Slovakia

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ABSTRACT

The effect of three samples of SNF FO grade cationic polyelectrolyte (PE) and two samples of SNF AN grade anionic polyelectrolyte as well as their binary mixtures on the electrokinetic potential of monodisperse carboxylated polystyrene (PS) particles as a function of the contact time of polymer solution with particles, the polyelectrolyte/mixture dose, its composition, the charge density (CD) of polymers and sequence of their adding to the suspension has been studied. Also the effect of pH and KCl concentration on the ζ-potential of "bare" and polymer-covered PS particles have been measured. It has been shown that addition of increasing amount of anionic polyelectrolytes increases the absolute value of the negative zeta-potential of PS particles; this increase is stronger the charge density of the polyelectrolyte and pH of the system are higher. Adsorption of cationic polyelectrolytes leads to a significant decrease in the negative ζ -potential and to overcharging the particles; changes in the ζ -potential are more pronounced for PE samples with higher CD and for suspensions with lower pH values. In mixtures of cationic and anionic PE, in a wide range of mixtures composition, the ζ -potential of particles is determined by the adsorbed amount of the anionic polymer independently of the CD of polyelectrolytes and the sequence of addition of the mixture components. The isoelectric point of the surface is reached at the adsorbed amount of positive charges that is approximately equal to the surface charge density of particles. The laws observed were explained by features of macromolecules conformation in adsorbed mixed polyelectrolyte layers. Considerations about the role of coulombic and non-coulombic forces in the mechanism of anionic/cationic polyelectrolyte adsorption are presented.

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1. Introduction

Measurements of the electrokinetic potential of dispersed particles in polyelectrolyte (PE) and PE mixture solutions represent interest from different points of view: (i) they provide information about the changes in the electrical double layer (EDL) structure in the presence of adsorbed macromolecules/macroions; (ii) they help to discriminate the coulombic and non-coulombic interactions in the mechanism of polyelectrolyte adsorption; (iii) they enable us to estimate the contribution of electrostatic and non-electrostatic forces in the mechanism of stabilization and destabilization of polyelectrolyte-containing dispersions; (iv) they help us to elucidate the mechanism of layer-by-layer deposition, i.e., building of polyelectrolyte multilayers which is a promising area for engineering new functional materials and sensors. A critical review on the problem is recently given by Lyklema and Deschenes [1]. The main features of polyelectrolytes adsorption on solid surfaces can be summarized as follows [1–9]. Adsorption of oppositely charged PE results in a decrease of the electrokinetic potential and overcharging the particles surface. By majority of authors it is attributed to strong, long range electrostatic attraction between opposite charges of the surface and the polyelectrolyte. At the same time the additional adsorption of polyelectrolytes after compensation of the surface charge cannot be explained purely by electrostatic interactions and a question about the role of non-electrostatic forces arises. Adsorption of PEs of the same charge in many cases leads to an increase of the zeta-potential of particles but in several systems no marked effects were registered. The adsorption is due to non-coulombic effects such as hydrophobic interactions, Hbond formation. There are several enigmatic/unsolved questions in this big problem: how the charge density of the polymer and the surface, i.e., the pH, as well as the solution ionic strength influence the adsorption of polyelectrolytes and its effect on the EDL structure, how to discriminate the contribution of electrostatic and non-electrostatic effects into mechanism of PE adsorption at different conditions, etc. Description of the EDL structure of soft surfaces composed of a hard particle with adsorbed polyelectrolyte layer (PEL) on it is not an easy task both from theoretical and

^{*} Corresponding author. Tel.: +36 46 565110; fax: +36 46 565110. *E-mail address:* akmbsab@uni-miskolc.hu (S. Barany).

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