Nanoparticles based on polyelectrolyte complexes: effect of structure and net charge on the sorption capability for solved organic molecules

Abstract The sorption of solved organic molecules such as p-nitrophenol or dyes on previously formed nanoparticles based on polyelectrolyte/micelle complexes or polycation/polyanion complexes was studied. It can be shown that the sorption capability strongly depends on the structure and properties of the complex particles. Investigations have been made with complex particles that differ in their hydrophobic/hydrophilic structure, size and net charge. Such complex aggregates could be prepared by mixing the cationic surfactant dodecylamidocetyltrimethylammonium chloride, the polycations poly(diallyldimethylammonium chloride) or poly(methacryloyloxyethyltrimethylammonium chloride) and the copolymers of maleic acid with propene or methylstyrene as anionic components. It is found that the sorption capability increases with increasing molar mass and hydrophobic properties of the components used. In addition, the concentration ratio \( c_{\text{polym}}/c_{\text{org, pol}} \) that was required to reach optimal sorption conditions could be decreased by the use of macromolecules with high molar masses. The best results were obtained by using cationic stabilized complex particles formed with high-molar-mass polycations as sorbents for anionic dye molecules.

Key words Polyelectrolyte complexes · Nanoparticles · Colloidal dispersions · Sorption · p-Nitrophenol

Introduction

Polyelectrolyte–colloid interactions have attracted considerable interest because of their importance for both biological phenomena (e.g. immobilization of enzymes and protein purification) and industrial applications (e.g. water purification and cosmetic and paint formulations).

The electrostatically driven interaction between the polyelectrolyte and oppositely charged micelles may represent the model system for Coulombic interaction of linear macroions and colloids. It could be shown that the charge density of the polyelectrolyte chains as well as the hydrophobicity of polymer backbones/surfactant tails can significantly affect the structures and properties of the polyelectrolyte/surfactant complexes (PSCs) [1, 2].

Concerning the dye solubilization in polyelectrolyte/micelle complexes a correlation was found between the solubilization capacity and cooperative binding in such systems [3–5]. According to Ref. [6] the removal of aromatic hydrocarbons or dyes from wastewater with PSCs is very effective if the components are able to form water-insoluble three-component complexes. The formation of such colloid aggregates of PSCs is also potentially important in colloid–enhanced ultrafiltration processes designed to remove both molecular organic solutes and organic ions present in contaminated aqueous streams [7, 8].

It is well known that highly aggregating systems are also formed if oppositely charged macromolecules interact with each other. The structure and properties of the polyelectrolyte complexes (PECs) formed are
determined by a number of factors: the characteristics of the polyelectrolyte components and their concentrations, the ratio between numbers of oppositely charged groups of polyelectrolytes as well as the conditions of the surrounding medium (e.g. ionic strength, pH, temperature).

PECs are of considerable interest because of their various potential applications. For instance, PECs were found to be promising flocculants for colloidal dispersions [9] and have also been successfully applied as efficient binders of dispersed dyes [10].

In previous work, concerning surface modification of silica particles and fibres with PECs [11, 12], we mixed oppositely charged polyelectrolytes in the presence of the substrate. During these experiments adsorption processes and polymer complexation take place simultaneously and therefore it was difficult for us to give a clear interpretation of the dependence of the resulting modification effect on the properties and stability of the PECs formed. In order to overcome these difficulties we used previously formed stable PEC dispersions [13]. Such stable colloidal dispersions that contain compact and nearly spherical nanoparticles are formed when charged groups of a cationic polyelectrolyte are taken in a certain excess compared with charged groups of an anionic polyelectrolyte. As an anionic polyelectrolyte we used copolymers of maleic acid with alkenes.

The aim of this work was to prepare PEC nanoparticles with different properties and characteristics, such as structure, size, hydrophobicity, net charge, etc., and to test these nanoparticles as sorbents for water pollutants. The idea is based on the fact that PECs and also PSCs contain both hydrophobic and hydrophilic molecular groups and therefore it is natural to expect that the complex particles can interact with charged and uncharged molecular organic solutes. For this study p-nitrophenol (p-NPh) and the anionic dye bromocresol green (BKG) were chosen as model pollutants.

**Experimental**

**Materials**

Stable dispersions of PECs were formed with oppositely charged macromolecules if one of these components was used in excess.

The polycations used were poly(diallyldimethylammonium chloride) (PDADMAC) with $M_n \approx 2.5 \times 10^5$ g/mol and poly(methacryloyloxyethyldimethylammonium chloride) (PMADAMBQ) with $M_n \approx 4.1 \times 10^5$ g/mol. Both polycations were synthesized and characterized by W. Jaeger (Fraunhofer Institut für Angewandte Polymerforschung, Teltow, Germany); details are described elsewhere [14, 15]. As a cationic surfactant dodecylamidoethylbenzlammonium chloride (commercial name Quartolan) obtained from Rodlben, Germany, was employed. The structures of the cationic components used are shown in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Cationic components used for complex formation</th>
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<tbody>
<tr>
<td>Dodecylamidoethyl dimethylbenzlammonium chloride Quartolan</td>
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<tr>
<td>Poly(diallyldimethylammonium chloride) P(DADMAC)</td>
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<tr>
<td>Poly(methacryloyloxyethyldimethylbenzlammonium chloride) P(MADAMBQ)</td>
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$$
\text{C}_{12} \text{H}_{25} \text{NH} - \text{C} - \text{CH}_2 \cdot \text{CH}_2 - \text{N}^+ \text{CH}_3
$$

$$
\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N}^+ \text{CH}_3
$$

$$
\text{C}_2 \text{H}_5 \text{O} - \text{N}^+ \text{CH}_3
$$

$$
\text{CH}_3 \text{CH}_2 \text{N}^+ \text{CH}_3
$$