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ORIGINAL CONTRIBUTION

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

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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 could 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 dodecylamidoethyldimethylbenzylammonium chloride, the polycations poly(diallyldimethylammonium chloride) or poly(methacryloyloxyethyldimethylbenzylammonium 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 $c_{\mathrm{polym}}/c_{\mathrm{org.poll}}$ 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 application (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.

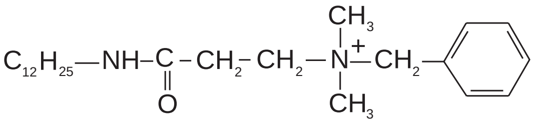
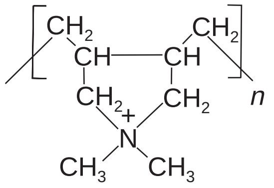
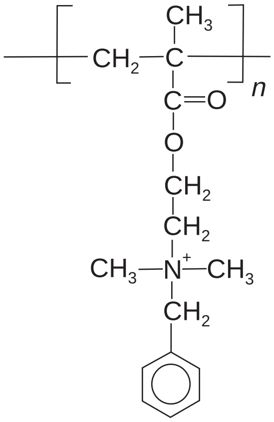
Experimental

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 $M_w \cong 2.5 \times 10^5$ g/mol and poly(methacryloyloxyethyldimethylbenzylammonium chloride) (PMADAMBQ) with $M_w \cong 4.1 \times 10^6$ 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 dodecylamidoethylbenzylammonium chloride (commercial name Quartolan) obtained from Rodleben, Germany, was employed. The structures of the cationic components used are shown in Table 1.

Table 1 Cationic components used for complex formation

Dodecylamidoethyldimethyl-benzylammonium chloride Quartolan	
Poly(diallyldimethylammonium chloride) P(DADMAC)	
Poly(methacryloyloxyethyldimethyl-benzylammonium chloride) P(MADAMBQ)	

Copolymers of maleic acid with propene [P(MS-P)] and α-methylstyrene [P(MS-α-MeSty)] were used as anionic polyelectrolytes. They were prepared by hydrolysis of the corresponding anhydrides with a solution of NaOH. These anhydrides with $M_w \cong 50\,000$ g/mol [P(MS-P)] and $M_w \cong 24\,000$ g/mol [P(MS-α-MeSty)] were obtained from Leuna, Germany.

The organic model pollutants p-NPh and the anionic dye BKG were used without further purification. Deionized water was employed as the solvent.

Preparation of stable dispersions of the complex nanoparticles

For the complex formation the stock solutions ($c = 5 \times 10^{-3}$ mol/l; pH = 6.0) of the oppositely charged polyelectrolytes were diluted and mixed under continuous stirring. In the experiments we put the solution of the excess component in the mixing vessel and the desired amount of the oppositely charged component was added dropwise to the stirred solution. The range of concentrations investigated was $c_{\text{polym}} = (5 \times 10^{-3} - 5 \times 10^{-4})$ mol/l. By changing the molar mass ratio between anionic and cationic charged units (n^-/n^+) in the mixtures, stable dispersions of complexes with different properties could be prepared. When an excess of free polyions (n^+ or n^-) is present, these polyions can stabilize and screen the complex particles formed. The prepared dispersions of cationic or anionic stabilized complex particles are stable with dimensions $R_h \cong 70$–150 nm.

Characterization of the complex dispersions

The stability of all the mixtures was checked by measuring the optical density (OD) at 500 nm. Deionized water was used as a reference (transmittance = 100%). The values of the OD were obtained with a Lambda 2 UV/vis spectrometer (Perkin Elmer, UK.)

All measurements were taken 1 h after mixing and were checked after 2 days.

Quasielastic light scattering measurements were performed at a scattering angle of 90° with a commercially available Zetasizer 3000 (Malvern Instruments, UK) equipped with a 10-mW He–Ne laser as a light source; the operating wavelength was 633 nm. Analysis of the autocorrelation function, $g^{(2)}(\tau)$, was done automatically to yield the mean diffusion coefficient, D_T, and thence, from the Stokes–Einstein expression, the apparent mean hydrodynamic radius, R_h.

Electron microscopic studies on the complex particles formed confirmed the spherical shape as well as the high polydispersity found by quasielastic light scattering [16].

Pollutant sorption

Visible spectrophotometry was used to monitor the uptake of p-NPh or BKG. For the sorption experiments 10 ml of the stable complex dispersions ($c_{\text{polym}} = 3.2$ mmol/l) was added to 15 ml of an aqueous solution containing different concentrations of p-NPh or BKG. The samples were sealed and intensively mixed at room temperature over a sorption time of about 3 h. After that the complex particles were separated from the solution by means of a membrane filter made from cellulose acetate with a pore size of 0.2 μm.

The concentrations of p-NPh and BKG in the filtrate were then determined by UV spectrophotometry (Lambda 2, Perkin Elmer, UK). Analyses of the p-NPh concentrations were performed at 400 nm after converting the p-NPh to the *p*-nitrophenoxide ion by adjusting the pH to a value of 9 using 1 mol/l NaOH. The uptake of the dye BKG was analyzed from the concentrations determined at 516 nm.

Results and discussion

Characteristics of the complex nanoparticles

Generally, PEC formation is mainly caused by the strong Coulombic interaction between the oppositely charged components. Under special conditions, aggregated complex particles can be prepared using polyelectrolytes with significantly different molecular weights at nonstoichiometric mixing ratios. In this case the PEC particles consist of highly densely packed cores, which are surrounded by polyions of the excess component [17, 18].

In connection with the use of such PEC particles as sorbents for solved organic molecules, we studied the influence of the total polymer concentration and the properties of the polyelectrolytes used on the behavior of the complex particles formed at the fixed molar ratio $n^-/n^+ = 0.5$ for the systems PDADMAC/P(MS-α-MeSty) and PDADMAC/P(MS-P).

Results concerning the size of the complex particles and the turbidity of the complex dispersions with respect to the polymer concentration are given in Figs. 1 and 2, respectively. Apart from the concentration effect showing an increase in the size of the complex particles with rising polymer concentration, we could also observe a clear influence of the molecular structure of the polyelectrolytes on the properties of the PECs formed. By use of P(MS-α-MeSty) the complex particles formed are larger than particles of PDADMAC/P(MS-P) and above a polymer concentration of about 3.5 mmol/l aggregation of the particles during a storage time of 2 days was observed. Since P(MS-α-MeSty) contains benzene groups while P(MS-P) does not, the bad steric fit between the oppositely charged polyelectrolytes may

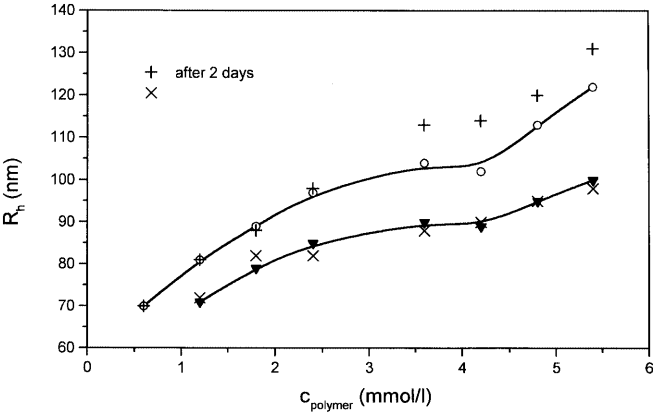


Fig. 1 Particle size versus total polymer concentration for mixtures of poly(diallyldimethylammonium chloride) (*PDADMAC*) and copolymers of maleic acid with methylstyrene [*P*(*MS*-α-*MeSty*)] (○) or with propene [(*MS-P*)] (▼), $n^-/n^+ = 0.5$

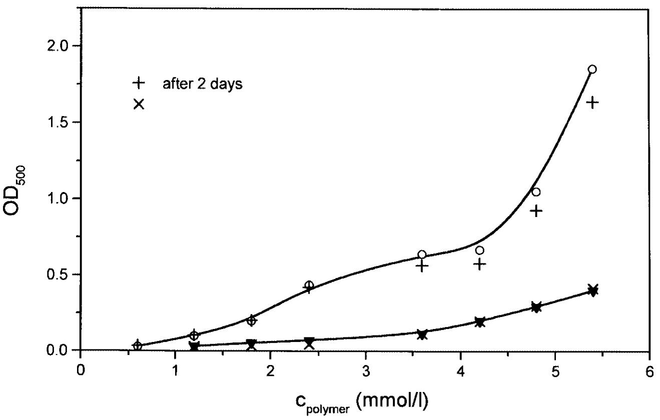


Fig. 2 Optical density of complex dispersions versus total polymer concentration for mixtures of PDADMAC/P(MS-α-MeSty) (○) and PDADMAC/P(MS-P) (▼), $n^-/n^+ = 0.5$

also support the observed stronger aggregation of the complex particles and the increasing destabilization of the complex dispersions formed with P(MS-α-MeSty). Taking into consideration that the values of the OD are influenced by the size, the number and the structure of the complex particles formed, the turbidity data can also be used to evaluate the stability and properties of the complex dispersions. As shown in Fig. 2 the values of OD_{500} obtained for the system PDADMAC/P(MS-P) are lower than those for PDADMAC/P(MS-α-MeSty) and they do not change with time.

The results obtained demonstrate that it was possible to prepare stable complex nanoparticles with both systems investigated.

Sorption studies

Firstly, sorption experiments were performed with stable complexes of PDADMAC with P(MS-α-MeSty) and P(MS-P). By changing the molar ratio n^-/n^+ and the excess component we could prepare both cationic stabilized and anionic stabilized complex particles. The structural parameters of the different PECs and the corresponding sorption data for p-NPh are given in Table 2.

From the results obtained by light scattering we could show that the complex particles generated differ in their sizes and structures. Also a high level of aggregation and a large polydispersity of the PEC particles were detectable. In order to explain this phenomenon we should take into consideration that during PEC formation the polyelectrolyte chains change via ionic binding from hydrophilic species to more hydrophobic ones, causing aggregation; however, excess binding of the major component, especially on the surface of the PEC particles, results in electrostatic stabilization, but a partial coagulation cannot be excluded in such complicated processes.

For our first sorption experiments we used complex particles of PDADMAC with P(MS-α-MeSty) and P(MS-P) prepared at different molar ratios. These particles differ in the size and charge of the shell-forming component. To determine the effectiveness of the different complexes we mixed solutions of the PEC particles and of p-NPh in a fixed concentration ratio $(c_{\mathrm{polym}}/c_{\mathrm{p\text{-}NPh}}) \cong 50$. As a result the PDADMAC/P(MS-α-MeSty) particles prepared at a molar ratio $n^-/n^+ = 0.6$ show a higher sorption capability compared to the PDADMAC/P(MS-P) particles at the same molar ratio. To explain this difference we should consider the size of the complex particles and also the properties of the shell-forming polyelectrolytes. In this case the complex particles formed with P(MS-α-MeSty), the more "hydrophobic" polyanion, are larger and more aggregated. Because of the larger surface of these particles we think that the number of polyions forming the shell also increases. If more PDADMAC molecules are incorporated into the shell then more p-NPh molecules can interact and, therefore, a higher sorption capability is detected.

On the other hand, the anionic stabilized complex particles prepared at a molar ratio $n^-/n^+ = 1.7$ show a drastic decrease in the sorption capability. This should be expected if we take into consideration that interactions between the anionic polarized p-NPh molecules and the anionic stabilized complex particles are prevented by electrostatic repulsion.

Sorption experiments were also performed with PECs formed by variation of the cationic component. Cationic stabilized complex particles were formed with Quartolan, PDADMAC and PMADAMBQ by mixing with P(MS-α-MeSty) as the polyanion at a molar ratio $n^-/n^+ = 0.6$. The sorption isotherms obtained by use of these complex systems are shown for p-NPh in Fig. 3

Table 2 List of the complexes formed with PDADMAC, their structural parameters and data of sorption

Polyelectrolyte complexes	n^-/n^+	R_h (nm)	Polydispersity	$c_{\mathrm{polym}}/c_{\mathrm{p\text{-}NPh}}$	Sorption capability ($\mathrm{mg_{p\text{-}NPh}/mg_{polym}}$)
PDADMAC/ P(MS-P)	0.6	78	0.15	50	0.006 ≅ 27%
PDADMAC/ P(MS-α-MeSty)	0.6	104	0.19	48	0.009 ≅ 38%
PDADMAC/ P(MS-α-MeSty)	1.7	82	0.20	53	0.003 ≅ 16%

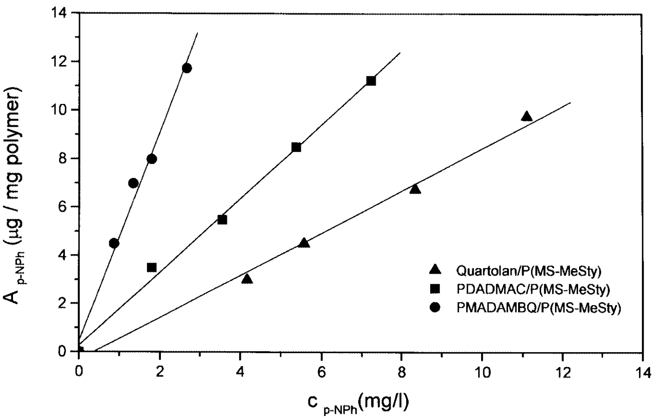


Fig. 3 Dependence of *p*-nitrophenol (*p-NPh*) absorption by the complex particles (n^-/n^+ = 0.6) on the initial concentration of p-NPh

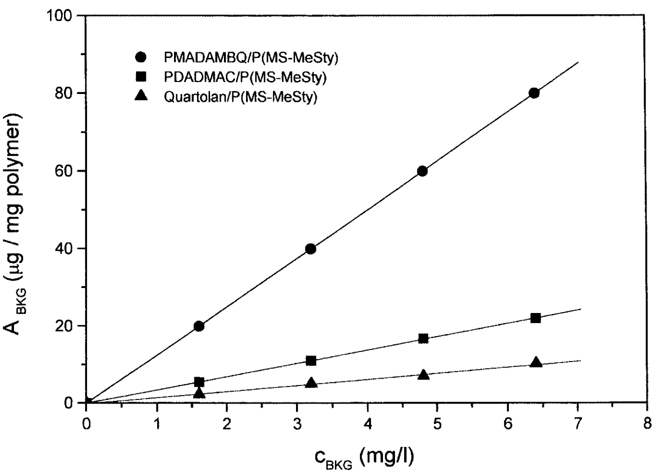


Fig. 4 Dependence of bromocresol green (*BKG*) absorption by the complex particles (n^-/n^+ = 0.6) on the initial concentration of BKG

and for the anionic dye BKG in Fig. 4. As can be seen from the plots the isotherms obtained can be described appropriately by straight lines with an intercept of zero.

The experiments were performed using the PECs in a large excess compared to the solved pollutant molecules. In order to evaluate the sorption capability of the different complex systems we used the slope of the isotherms obtained under the same experimental conditions.

It was found that the slopes essentially increase with increasing molar mass of the major cationic component used. From a quantitative comparison of the slopes obtained with the different complexes for both p-NPh and BKG (Table 3), the following correlation between sorption capability, structure of the major cationic component used and properties of the complex particles could be shown: by exchanging Quartolan with PDADMAC in the complexes the slope of the isotherms was about doubled and by exchanging PDADMAC with PMADAMBQ a roughly threefold increase of the slope was observed.

Table 3 Slopes of sorption isotherms of *p*-nitrophenol (*p-NPh*) and bromocresol green (*BKG*) obtained for different complex systems

Polyelectrolyte complexes ($n^-/n^+ \cong 0.6$)	Slope of isotherm (ml/mg polymer)	
	p-NPh	*BKG*
Quartolan/ P(MS-MeSty)	0.87	1.58
PDADMAC/ P(MS-MeSty)	1.55	3.45
PMADAMBQ/ P(MS-MeSty)	4.35	12.5

In addition the structural parameters of the cationic stabilized PECs and the corresponding sorption data obtained for p-NPh and BKG are summarized in Table 4. As shown the sorption capabilities of the different complex systems are higher for BKG than for p-NPh. This is reasonable because additional strong ionic interactions can act between the charged groups of the anionic dye molecules and the cationic net charges of the complex particles. The results also indicate that independent of the properties of the solved organic molecules the sorption capability of the surfactant/polyelectrolyte complex is smaller than of the complexes formed with polycations as the major component. In connection with this it is also important to note that the concentration of the Quartolan/P(MS-α-MeSty) complex employed in order to reach a comparatively high sorption was about twice as high as for the interpolyelectrolyte complexes used.

For the interpretation of the experimental results obtained it is important to discuss the structure and properties of the complex particles formed with respect to the properties of the oppositely charged components and the mixing conditions. The formation of the charge-stabilized and aggregated complex nanoparticles is assumed to be the result of the processes depicted schematically in Fig. 5.

The scheme given for cationic surfactant/polyanion points out the possibility for polyelectrolyte chains to connect micelles. The micelles are formed in aqueous solution at a surfactant concentration higher than the critical micelle concentration (cmc). In this model the micelles formed have a hydrophobic core and a hydrophilic cationic charged corona. By addition of the oppositely charged polyelectrolyte the micelles were bridged via electrostatic interactions and polyelectrolyte/micelle aggregates with three-dimensional, ordered structures can be formed.

For polycations/polyanions the formation of the multicomplex aggregates is illustrated schematically in the lower half of Fig. 5. At first, oppositely charged macromolecules interact spontaneously and form

Table 4 List of the complexes prepared by variation of the cationic component, their structural parameters and data of sorption for p-NPh and BKG

Sorption of p-Nph

Polyelectrolyte complexes	n^{-}/n^{+}	R_h (nm)	Polydisp.	$C_{poly}/C_{p\text{-}NPh}$	Sorption capability ($mg_{p\text{-}NPh}/mg_{polym}$)
Quartolan/ Poly(MS-α-MeSty)	0.6	130	0.14	80	0.004 ≅ 36%
PDADMAC/ Poly(MS-α-MeSty)	0.6	104	0.19	48	0.009 ≅ 38%
PMADAMBQ/ Poly(MS-α-MeSty)	0.6	140	0.53	30	0.012 ≅ 40%

Sorption of BKG

Polyelectrolyte complexes	n^{-}/n^{+}	R_h (nm)	Polydisp.	C_{poly}/C_{BKG}	Sorption capability (mg_{BKG}/mg_{polym})
Quartolan/ Poly(MS-α-MeSty)	0.53	146	0.15	90	0.007 ≅ 68%
PDADMAC/ Poly(MS-α-MeSty)	0.53	95	0.17	50	0.017 ≅ 84%
PMADAMBQ/ Poly(MS-α-MeSty)	0.6	145	0.53	25	0.04 ≅ 100%

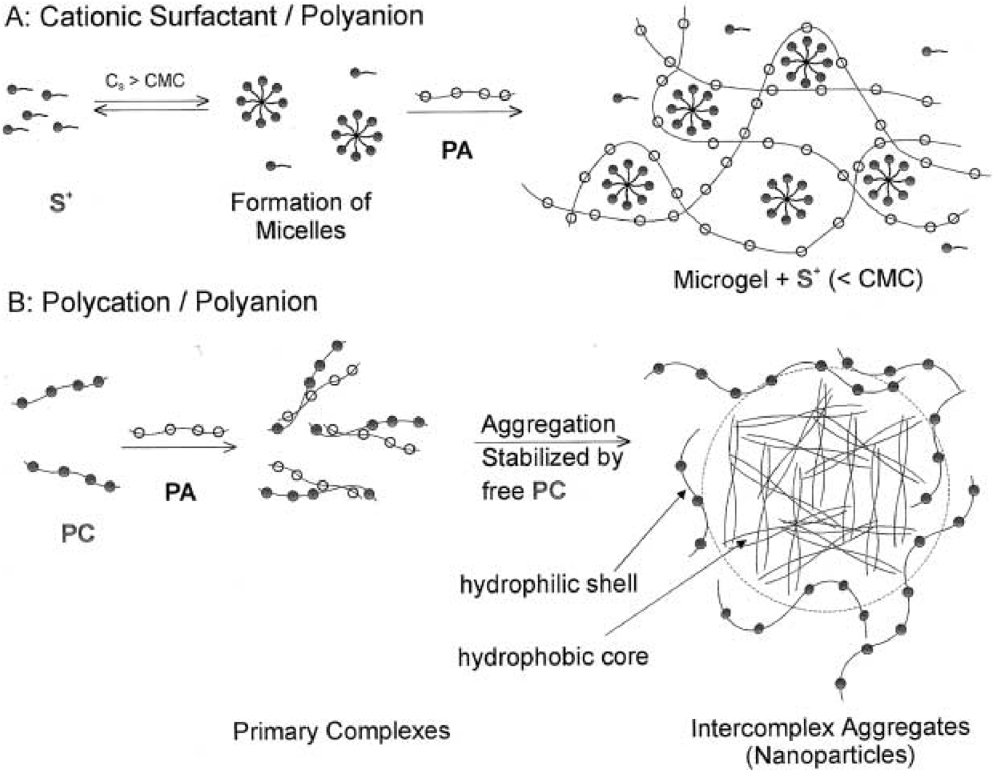


Fig. 5 Scheme of the formation of nanoparticles by polyelectrolyte/micelle complexes (*A*) and interpolyelectrolyte complexes (*B*)

primary macromolecular complexes. In aqueous solution, such assemblies can undergo progressive aggregation via hydrophobic interactions and as a result multicomplex aggregates are formed. In addition the free cationic macromolecules, used as the major component in this model system, can be absorbed onto surfaces of the multicomplex aggregates that become similarly charged. This process counteracts further aggregation, and, as a result, PEC nanoparticles of a "core–shell" structure with a hydrophobic core and a hydrophilic shell formed by loops and tails of the absorbed macromolecules are assumed to appear.

On the basis of the models developed concerning the structure of the complex aggregates, we are able to discuss and to understand better the experimental data reported in this work. We could show that the properties of the PEC nanoparticles can be controlled by the "shell–forming" polyelectrolytes. Thus, the use of polyelectrolytes with a high molar mass and high charge density (e.g. PMADAMBQ) in excess promote the buildup of shells with an extended structure stabilized by loops and tails of the major component bearing the net charges. As a consequence and in good correlation with our sorption data, the sorption capability of the complex particles increases with increasing molar mass of the polycations used.

On the other hand, by use of polyelectrolyte/micelle complexes as sorbents, the values of sorbed amounts obtained related to the polymer concentration were smaller for both solved molecules p-NPh and BKG. Considering these results it is not so easy to understand that the polyelectrolyte/micelle-complexes investigated differ so clearly in their sorption properties from the colloidal particles of the PECs tested. A possible reason may be that we used the cationic surfactant Quartolan as the major component and at a concentration above the cmc: a cmc of 1.5 ± 0.2 mmol/l was obtained from surface tension measurements.

Based on a stoichiometric aspect at the formation of polyelectrolyte/micelle complexes, the fraction of micelles in the bound state is determined by the concentration and properties of the polyions. In our studies we used the polyanion as the minor component and under these conditions not all the micelles were bound to the polymer. Considering the fact that the sorption efficiency of micelles is mainly determined by their shape and structure independently of their bound state, in our experiments both polyelectrolyte/micelle complexes and also free micelles can act as sorbents for solved organic molecules. To determine the sorption capability of the different complex systems we removed the unsorbed solved molecules by filtration. By this procedure only the aggregated complex particles and not the free micelles could be separated from the solution. As a consequence the calculated values of the quantity of sorbed organic molecules are too small because the number of micelles also containing sorbed organic molecules could not be exactly determined in the filtrate.

To elucidate this effect additional sorption experiments will be realized using polyelectrolyte/micelle complexes in which the polyion is in large excess. These conditions should ensure that virtually all the micelles formed are bound to the polyions and therefore a complete separation may be possible.

Conclusions

Stable dispersions of PEC nanoparticles can be used to remove solved organic molecules from aqueous solution via hydrophobic or electrostatic interactions. It could be shown that the sorption capability of such macromolecular assemblies increases with increasing molar mass and hydrophobic properties of the macromolecules used. The concentration ratio PEC dispersion/solved organic molecules that was required to reach optimal sorption conditions decreased by using macromolecules with high molar masses. The best results were obtained for the cationic stabilized complex system P(MADAMBQ)/P(MS-α-MeSty) and the anionic dye BKG.

The practical aspects of the present research are connected with the design of new materials for removing organic pollutants from wastewater.

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