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Joachim Koetz · Sabine Kosmella

Polyelectrolytes and Nanoparticles

With 36 Figures and 6 Tables

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Prof. Dr. Joachim Koetz
Universität Potsdam
Institut für Chemie, Professur für Kolloidchemie
Karl-Liebknecht-Straße 24/25, Haus 25, Raum D/2.19
14476 Golm
Germany
e-mail: koetz@rz.uni-potsdam.de

Dr. Sabine Kosmella
Universität Potsdam
Institut für Chemie
Karl-Liebknecht-Straße 24/25, Haus 25, Raum D/2.19
14476 Golm
Germany
e-mail: kolloid@rz.uni-potsdam.de

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Dedication

After surviving a plane crash on March 6, 2005, in the Alps, I started to write this book, which is dedicated to my father Gottfried, my wife Sybille, my two daughters Theresa and Stephanie, as well as to my aviation friends Boris, Ingolf, and Peter.

Joachim Koetz

Preface

Polyelectrolytes, i.e., water-soluble polymers with a lot of dissociating functional groups, and nanoparticles, i.e., fine particles with diameters on the nanometer scale, are two substance classes of growing interest. Both polyelectrolytes and nanoparticles can be found in many industrial applications such as in paints, paper coatings, cosmetics, and pharmaceuticals. For adjusting the properties of such multicomponent systems, the knowledge of the macromolecular and electrochemical features of the polyelectrolytes on the one hand, and the size and shape of the nanoparticles on the other hand is essential.

Understanding the basic principles involved in the preparation of nanoparticles and control of the interparticle interaction forces by adsorbing polyelectrolytes is therefore crucial, both from a scientific and application oriented point of view.

Over the last years, the term nanotechnology, which refers to the technology that produces nanosize particles, has been established, and a new fast-growing market has been born. The pioneers in this field were the alchemists, who were already able in the 16th century to produce colloidal gold, however, without knowledge of the scientific background of the formulation process. Today, of course, we know much more about the colloidal metal nanoparticles, but still some questions are open. Therefore, especially the formation, characterization, and stabilization of gold nanoparticles as a nanoscalic model system in presence of polyelectrolytes, is discussed here in more detail. Polyelectrolytes can play an important role with regard to the formation and stabilization of nanoparticles with diameters smaller than 10 nm, which is of special interest with regard to new fields of application.

The purpose of this book is to outline synergistic effects between polyelectrolytes and nanoparticles to show new ways of synthesis and to present methods to characterize well-defined polyelectrolyte-modified nanoparticles.

This book originates from the lecture and laboratory course of the Polymer Science Program at the University of Potsdam (Institute of Chemistry), and is expanded by topics from lectures and experiments in colloid chemistry. The book will be useful for graduate students and postgraduates of polymer and colloid science or research and industrial chemists, physicists, or engineers working in related areas of material or life sciences.

In a comprehensive manner, the book combines the basic principles of the characterization of water-soluble polyelectrolytes with their ability to control the nanoparticle formation process and/or to stabilize the nanoparticles due to an adsorption on the particle surface.

Potentiometric techniques are used to characterize phenomena of counterion condensation, the nature of interactions with oppositely charged surfactant molecules as well as the stoichiometry of polyelectrolyte complexes. Zeta-potential measurements are carried out to detect the adsorption of polyelectrolytes on the nanoparticle surface. For characterizing the shape and size of the nanoparticles, dynamic light-scattering measurements can be successfully used in combination with transmission and/or scanning electron microscopy (SEM). The different preparation techniques are outlined and experimental details are described.

We would like to express our sincere thanks to Dr. Brigitte Tiersch for her EM contribution to the book including the TEM and SEM micrographs and we would also like to thank the members of our workgroup involved in this project. Furthermore, we want to thank Prof. Burkart Philipp for introducing us to the still-fascinating field of polyelectrolytes and polyelectrolyte complexes; Prof. Stig Friberg and Prof. Raymond Mackay for introducing us to self-assembled template phases, and Prof. Keisheiro Shirahama for surfactant-selective electrodes. The fruitful cooperation with Prof. Markus Antonietti from the Max Planck Institute on the other side of the railway in Golm is gratefully acknowledged, and finally, the authors give thanks to Prof. Werner-Michael Kulicke and Dr. Harald Pasch for encouraging us to write this book.

Potsdam, December 2005

Joachim Koetz
Sabine Kosmella

List of Symbols and Abbreviations

a	Exponent of the KMHS equation
A_2	Second virial coefficient of the osmotic pressure
AOT	Sodium bis(2-ethylhexyl)sulfosuccinate
ATRP	Atom transfer radical polymerization
b	Spacing between two charged groups
b_{gf}	Geometric factor
c	Concentration
$c_{cat,t}$	Total concentration of polycation repeat units
$c_{cat,f}$	Concentration of free polycation repeat units
$c_{cat,b}$	Concentration of the complexed polycation repeat units
C_{sa}	Spherical aberration coefficient
C_{H^+}	Molar concentration of H^+ ions
C_{PEL}	Molar concentration of the polyelectrolyte
C_{exp}	Experimentally given counterion concentration
C_{tot}	Total counterion concentration
CTAB	Cetyltrimethylammonium bromide
cmc	Critical micellization concentration
CMC	Carboxymethylcellulose
d	Particle diameter
d_p	Resolving power of a microscope
d_{th}	Theoretical resolution of two points
D	Diffusion coefficient
DLS	Dynamic light scattering
DS	Degree of substitution
e	Elementary charge
emf	Electromotive force
E	Amplitude of the electric field
E_o	Applied electric field
E_s	Streaming potential
ESA	Electrokinetic sonic amplitude
$f(\kappa a)$	Henry function
$g_1(\tau)$	Correlation function of the electric field
$g_2(\tau)$	Intensity-time correlation function
$g(n)$	Free energy of an aggregate
g^b	Free bulk energy

g^s	Free interfacial energy
G_A	Energy to expand the interface
G_B	Interfacial bending energy
G_I	Free energy of interaction
G_{SH}	Free energy of interfacial sheath structure
ΔG_{el}	Electrostatic work
ΔG	Free energy change
H	Mean curvature
H_o	Spontaneous curvature
I	Ionic strength
I_c	Conduction current
I_{ss}	Streaming current
I_e	Effective ionization
I_o	Intensity of light
I_s	Scattering intensity
$I_{\phi o}$	Scattering intensity integrated over the whole sphere area
I_c	Conduction current
k	Boltzmann constant
K	Intrinsic constant for binding
K_a	Acidity constant
K_{as}	Association constant
K_{KMHS}	Constant of the KMHS equation
K_v^*	Constant for vertical polarized light
KPS	Potassium peroxodisulfate
m	Number of binding sites
M_n	Number average molar mass
M_w	Weight average molar mass
MA	Maleic acid
n, N	Number
N_2	Number of particles
N_G	Number of polycation repeat units
N_S	Number of polyanion repeat units
n^b	Number of bulk molecules
n^s	Number of surface molecules
n_o	Refractive index
n_{cat}	Average number of bound polycations per polyanion
Na-CMC	Sodium carboxymethylcellulose
Na-PAA	Sodium polyacrylate
Na-PSS	Sodium polystyrene sulfonate
$P(\vartheta)$	Debye scattering function
pK_a	Acidity constant
pK_b	Basicity constant
pK_{app}	Apparent acidity constant
pK_a^o	Intrinsic acidity constant

pH	Negative decadic logarithm of the H^+ ion activity
pH_{iso}	Isoelectric point
ΔpK	Deviation between the apparent and the intrinsic pK value
Δp	Pressure difference
PAA	Poly(acrylic acid)
PCS	Photon correlation spectroscopy
PDMAM	Poly(dimethylacrylamide)
PDADMAC	Poly(diallyldimethylammonium chloride)
PEC	Polyelectrolyte complex
PEI	Poly(ethyleneimine)
PEL	Polyelectrolyte
PEO	Poly(ethylene oxide)
PMA	Poly(methacrylic acid)
PSS	Poly(styrene sulfonic acid)
PVC	Poly(vinyl chloride)
PVP	Poly(vinyl pyridine)
Q	Magnitude of the scattering vector
Q_{pc}	Particle charge
QELS	Quasi-elastic light scattering
r	Radius
$R_{\vartheta,v}$	Reduced scattering intensity for vertical polarized light
R_h	Hydrodynamic radius
R_c	Critical radius
$[r^2]_z$	Radius of gyration
RAFT	Reversible addition-fragmentation chain transfer polymerization
SEC	Size exclusion chromatography
S_o	Shear plane
S_e	Sedimentation constant
SB	Surfactant with a sulfobetaine head group
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
t	Time
T	Thermodynamic temperature (in K)
TEM	Transmission electron microscopy
u	Parameter of cooperativity
V	Amplitude of the acoustic wave
V_h	Hydrodynamic volume
V_s	Solute volume
v^*	Partial specific volume
x	Molar fraction of acidic groups
x/x^{sat}	Supersaturation
z	Valence of counterion
Z	Partition function
α	Polarizability

α'	Degree of neutralization
α	Degree of dissociation
β	Degree of binding
ε	Bulk dielectric constant
γ	Surface tension
ϑ	Scattering angle
$[\eta]$	Intrinsic viscosity
η_{p}	Polymer viscosity
η_{s}, η_{o}	Solvent viscosity
η_{red}	Reduced viscosity
η_{sp}	Specific viscosity
φ	Degree of complexation
λ	Wave length
λ_{B}	Bjerrum length
λ_{o}	Conductivity
μ_{E}	Electrophoretic mobility
μ	Electrochemical potential
μ^{o}	Standard potential
μ^{b}	Chemical potential in the bulk phase
ν	Flow velocity
π	Osmotic pressure
θ	Degree of condensation
ϱ	Density
σ	Activity coefficient of the free fraction of counterions
σ_{ss}	Specific surface
τ	Correlation time
ω	Angular frequency
ξ	Charge density parameter (Manning parameter)
ξ^{o}	Rigidity parameter
Ψ	Electrostatic potential
ζ	Zeta potential
∞	Infinite

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