The Effect of Cross-Linking on the Frictional Behavior of Polyzwitterionic Brushes

Iuster Noa(1), Tairy Odeya(1), Kampf Nir(1), Klein Jacob(1)

(1) Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel

Polymer chains tethered at one end to a substrate are known as polymer brushes and can provide a robust and stable modification layer for obtaining desired surface properties. pMPC (poly 2-methacryloyloxy ethyl phosphoryl choline) is a unique biocompatible polymer that contains the PC unit as a zwitterionic side-group on the backbone of the polymer chain [1]. Here we describe the preparation of pMPC brushes grown from pre-initiated mica surfaces and cross-linked using EGDMA (ethylene glycol dimethacrylate). Brushes and cross-linked brushes of pMPC were grown in an oxygen free aqueous solution by using Atom Transfer Radical Polymerization (ATRP) for surface force balance (SFB) measurements [2]. In this project, we examined the variation of the friction force as a function of the shear velocity. It is known that the frictional behavior of polymer brushes is independent of the shear velocity [3]. However, once the brushes are cross-linked the frictional behavior changes and becomes dependent on the shear velocity. We were able to measure the friction forces using the SFB and detect the difference in frictional properties between the polymeric brushes and the cross-linked ones. This difference in the dependence of the friction force on the shearing velocity can be explained by the self-regulating mechanism of the interpenetration length of the brushes [3].


Interfacial Forces and Surface Morphology of Layer by Layer Complexes

Gaisinskaya Anastasia(1), Kampf Nir(1), Klein Jacob(1)

(1) Materials and Interfaces, Weizmann Institute of Science, Rehovot.

A systematic study of normal and shear forces between layer by layer (LBL) polymers complexed with different inclusions was performed. We studied the forces between different LBL complexes as a function of different materials and different amounts of adsorbed layers. The investigated polymers were chitosan and alginate, and these LBL polysaccharide complexes could maintain their integrity up to high pressures (P>120 atm), and exhibit interesting time-dependent effects. In addition, we studied the surfaces morphology of these complexes by atomic force and cryo-scanning electron microscopies. The results will be presented at the meeting.
Examining Role of Different Macromolecules In Biological Lubrication

Zhu Linyi (1, 2), Seror Jasmine (1), Kampf Nir (1), Klein Jacob (1)

(1) Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel
(2) Key Laboratory of Colloid and Interface Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

The ultralow friction coefficients between the articular cartilage surfaces in human hips or knees play an important role in supporting human daily activities. Breakdown of this lubrication can lead to osteoarthritis, which is one of the common joint dysfunction and affects a very large portion of the population in the world. Hyaluronic acid (HA) is present at the surface of articular cartilage at high concentrations. We are extending earlier work to investigate HA using a surface force balance (SFB), by constructing bHA-avidin-mica coating, and in addition examining how complexing of these layers with different materials may affect their lubrication. Results will be presented at the meeting.
Lubrication by Polymer Brushes: The Role of the Phosphatidylcholine Unit

Tairy Odeya (1), Kampf Nir (1), Armes Steven (2), Klein Jacob (1)

(1) Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel
(2) Department of Chemistry, University of Sheffield, Sheffield, United Kingdom

The Phosphatidylcholine (PC) unit is the most common head group of the phospholipids constituting artificial liposomes and of lipids extracted from the synovial fluid, and is the group exposed at the outer surface of liposomes composed of these lipids. Poly [2-(Methacryloyloxy) ethyl Phosphoryl Choline] (pMPC) is a unique biocompatible polymer that contains the PC unit as a zwitterionic side-group on the backbone of the polymer chain [1]. Brushes of the biomimetic pMPC were grown on macroinitiator-coated mica surfaces in an oxygen free aqueous solution by using Atom Transfer Radical Polymerization (ATRP) for surface force balance (SFB) measurements [2]. Shear force measurements yielded friction coefficients in the order of $\mu \sim 10^{-4}$-$10^{-5}$ at compressions of up to $\sim 10$MPa (100 atmospheres) across water and 0.2M salt solutions [3], and moreover we were able to characterize the brush height, adsorbance and surface density as a function of the growth conditions. We attribute this excellent lubrication performance to the hydration of the pMPC, with each PC side-group being hydrated by up to 15 or more water molecules behaving fluidly under shear motion.

Measurement of Hydrodynamic Thickness of Polyelectrolyte Brushes

Peretz Reut(1), Kampf Nir(1), Silbert Gilad(1), Klein Jacob(1)

(1) Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel

Several studies have explored the intrinsic structure and properties of polyelectrolyte brushes as a function of grafting density, charge density and ionic strength.

However, in these measurements it is often difficult to separate the effects of steric from those of long-ranged electrostatic interactions. It is therefore challenging to characterize the thickness of polyelectrolyte brush layer in aqueous solution. In this study we overcome this by extending the technique of the SFB (Surface Force Balance) to carry out measurements of the unperturbed hydrodynamic thickness of the brushes. We do this by applying a sinusoidal motion on the upper surface in the normal direction and while the surfaces approach each other, due to hydrodynamic coupling, their surface separation will oscillate with decreasing amplitudes. By this damping in amplitudes we deduce the hydrodynamic thickness without applying strong forces that might deform the material.

In this work we estimate the hydrodynamic thickness of a negatively charged polymer brush composed of diblock copolymer poly[methyl methacrylate]-block-poly[sodium sulfonatedglycidyl methacrylate] (PMMA-b-PSGMA). These copolymers are attached to each hydrophobized surface by their hydrophobic PMMA moieties with the non-adsorbing polyelectrolytic PSGMA tails extending into the aqueous medium to form a polyelectrolyte brush.

Our preliminary results show that the hydrodynamic thickness measured is consistent with a simple theoretical model for the brush thickness.
Molecular Origins of Biological Lubrication

Seror Jasmine (1), Yulia Merkher (2), Kampf Nir (1), Collinson Lisa (3), Day Anthony (3), Maroudas Alice (2), Klein Jacob (1)

(1) Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel
(2) Biomedical Engineering, Technion Institute of Technology, Haifa, Israel
(3) Faculty of Life Science, Wellcome Trust Center for Cell-Matrix Research, University of Manchester, Manchester, United Kingdom

Mammalian synovial joints such as hips and knees are extremely efficient lubrication systems reaching friction coefficient as low as 0.001 at high pressures (up to 100 atm) and shear rates (up to 106-107Hz); indeed, they are the most efficiently lubricated systems known in nature. However, despite much previous work, the exact mechanism responsible for this behavior is still unknown. In this work we study the molecular mechanism of synovial joint lubrication by emulating the articular cartilage superficial zone structure. Charged macromolecules extracted and purified from bovine hip joints using well known biochemical techniques and characterized with several methods have been studied when adsorbed on the surface of molecularly smooth mica. Using a surface force balance (SFB), normal and shear interactions between two surfaces mimicking the cartilage superficial layer have been examined in a systematic and controlled manner, focusing in particular on the frictional forces. The implications of our results for understanding biological lubrication will be described at the meeting.
Novel Hemo-and Enterosorbents Based on Lignin

Chopabayeva Nazira (1), Mukanov Kanatbek (1), Tasmagambet Amandyk (2)

(1) Laboratory of Engineering Profile, Kazakh National Technical University, Almaty, Kazakhstan
(2) Laboratory of Ion-Exchange Resins and Membranes, Institute of Chemical Sciences, Almaty, Kazakhstan

At present use of renewed sources of raw materials for creation of novel functional biomaterials is perspective for development of science and technique. We have developed novel nano- and macroporous ion-exchangers based on renewable natural raw material by two-step process including catalytic α-alkylation of hydrolyzed lignin by epoxide resin ED-20 and followed by amination of formed α-oxide derivative with the help of polyethyleneimine (PEI) and polyethylenepolyamine (PEPA). The optimal conditions of synthesis, composition, structure and physical chemical properties of nano-, macroporous ion-exchangers were investigated by FTIR, SEM, TEM, XRD, DSC and porosimetry methods. Textural characteristics of natural polymeric materials and sorbents were also studied. The results show that alkaline activation and modification of natural biomaterials leads to an increase in surface area and enhancement of mesoporosity. Maxima of mesopore size distribution curves shifted from 2.27 nm (extracted sample) to 4.17 and 5.28 nm (activated and modified samples respectively) indicating the increase of mesopore by a factor of 1.8-2.3. The modified sorbents mainly contained a pore size of 10.56 nm. Existence of sorption-active mesopores and transporting macropores in ion-exchangers plays important role in sorption, selectivity and kinetic properties of synthesized ion-exchangers.

Mechanical durable and pH resistant ion-exchangers with amine ligands, grafted on lignin, are used for removal of water- and lipidsoluble toxic metabolites from pathological blood serum of diabetic retinopathy patients. After contact with sorbents the total cholesterol level and average concentration of LDL-C, VLDL-C decreased to the level of optimum compensated diabetes (<4.8–6.0 mmol/L, <3.0–4.0 mmol/L respectively). The degree of HDL-C extraction insignificantly decreased from 0.68 to 0.47 mmol/L. Purification of serum blood proceeded not only by removal of atherogenic fractions of cholesterol, but also by adsorption of large amounts of triglyceride (TG) and glucose. After hemosorption the concentration of TG decreased from 3.14 mmol/L to 1.71–1.89 mmol/L that corresponds to level of optimum compensated diabetes (<1.7–2.2 mmol/L). The most indicative criteria of biological liquid detoxification from lipid substances is cholesteric index of atherogenicity. Its value is significantly decreased from 10.81 to 8.33 after contact of serum with samples. This is caused by the high adsorption degree of atherogenic fractions of cholesterol and a very low degree of HDL-C removal. As a result of effective uptake of glucose its content decreased from pathological levels (7.50 mmol/L) to 5.2 – 6.1 mmol/L that corresponds to physiological norm (< 4.2 – 6.1 mmol/L). Considerable hypolipidemic and hypoglycemic effects of nano-, macroporous ion-exchangers have potential application in medicine, biology and biotechnology as immune-stimulating and organ-protection agents. They can be used as hemo-, enterosorbsents for detoxification and purification of biological liquids including the metabolic treatment of diabetes, decreasing risks of diabetic retinopathy and normalization of the carbohydrate/lipid status of organisms.
Chitosan-DNA complexes: charge inversion and DNA condensation

Sennato Simona (1), Domenici Fabio (1), Bomboi Francesca (1), Sarti Stefano (1)

(1) Physics Roma, Sapienza University of Rome, Italy

The design of biocompatible PE complexes (PECs) is a promising strategy for in vivo delivery of biological macromolecules such as proteins and DNA. Particularly, the condensation of DNA by polycations (with the formation of the so called "polyplexes") received considerable attention for its potential in gene delivery applications, where the development of safe and effective non-viral vectors remains a central challenge. Among polymeric polycations, chitosan, derived by deacetylation of the naturally occurring polysaccharide chitin, has recently emerged as a suitable material for the preparation of non-viral gene delivery vectors. In this study, we compare the observed aggregation behavior of Chitosan-DNA complexes in different conditions with the predictions of existing models for the complexation of oppositely charged polyelectrolytes. We show that these models represent a consistent "frame" for different observations reported in the literature that previously appeared uncorrelated, and that they can hence be used as a guide to the rational design of new and more efficient polycation-based vectors, for an effective delivery of genetic material.
Dielectric Spectroscopy determination of Polyelectrolyte-Water interaction and hydration in semidilute solution

Sarti Stefano (1), Sennato Simona (1)

(1) Physics, Sapienza University of Rome, Roma, Italy

We present a detailed experimental study of Sodium Polyacrylate (Na-PA) dissolved in water as a function of concentration, in the semidilute regime and temperature. By measuring the amplitude and characteristic time of the relaxation of bulk water, we are able to identify and quantify the amount of water interacting with the polymer chains (bound water) and to follow its evolution as a function of temperature.
Swelling Characteristics of Electroactive Composite Systems Based on Acrylamide, Acrylic Acid and Polyaniline

Kabdrakhmanova Sana (1), Shaymardan Esbol (1), Zhilkashinova Almira (1)

(1) National Research Laboratory, S. Amanzholov East Kazakhstan State University, Ust-Kamenogorsk, East-Kazakhstan region, Kazakhstan

Recently, works are being widely carried out on the conducting polymers, so-called synthetic metals, to create nodes of fuel cells [1-3]. A number of works indicate the possibility of using polymers with electron-proton conductivity, such as polyaniline (PANI), to improve the effectiveness of platinum catalysts [4]. High level of electronic conductivity in combination with proton conductivity was indicated in polyaniline, which is critical in electrochemical processes associated with the simultaneous transport of protons and electrons. However, poor mechanical properties, poor water solubility and high melting point of polyaniline are a deterrent to use them.

In order to obtain elastic materials based on brittle polyaniline synthesis of composition systems was carried out by immobilizing the aniline in a hydrogel matrix of acrylamide (AAM) and acrylic acid (AA) of 3:1 mol/mol, respectively, which provides the required strength of material. The aim of this work was to study the kinetics of swelling of electroactive composites in water and aqueous media with different pH.

Synthesis of AAM-AA/PANI composite consisted of two stages, the first of which was receiving the polymer network of acrylamide and acrylic acid monomer and sorption of monomer by hydrogels of different concentrations (0.05-0.5 mol/L), and the second stage was polymerization of aniline by solution of ammonium peroxydisulfate (APS). The weight content of electrically conductive component, polyaniline, determined gravimetrically showed that the increasing of concentration of aniline from 0.05 to 0.15 mol/L leads to an increase in the content of conductive polymer in studied composite systems. When the concentration of aniline is 0.175-0.5 mol/L, the decrease of the content of polyaniline, which suggests the occurrence of changes in the structure of the mesh matrix AAM-AA during the formation of an electrically conductive component in it.

Degree of swelling in water and acid was measured and swelling kinetics of the pH value was studied for all of the composites. Since the degree of swelling of composites with a high concentration of polyaniline (0.05-0.5 mol/L) was significantly higher than initials, which were 0.14-0.2 g/g vs. 0.09 g/g of hydrogels without polyaniline. This proves the assumption of destruction of gel base of composition systems underwent to polymerization using APS [4]. Decrease of swelling ability of composites was noticed with increasing of concentration of aniline (0.4-0.5 mol/L). Perhaps this is due to the mechanical properties, i.e. brittleness of conductive gel.

It was shown that the degree of swelling of electroactive hydrogels sharply increases in alkaline media with pH increase, it is also possible due to the destruction of the mesh structure.

It was found that the nature and concentration of the conductive polymer has a significant impact on the structure of hydrogels of acrylamide and acrylic acid.

References
Ion transport in polyelectrolyte-modified nanopores

Tagliazucchi Mario (1), Rabin Yitzhak (2), Szleifer Igal (1)

(1) Department of Biomedical Engineering, Department of Chemistry and Chemistry of Life Processes Institute, Northwestern University, Evanston, Illinois, USA
(2) Department of Physics and Institute for Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan, Israel

This work introduces a molecular theory to study ion transport in nanochannels and short nanopores modified by end-grafted polyelectrolytes. The theory explicitly considers the coupling between the conformations of the polyelectrolyte chains, the electrostatic and non-electrostatic interactions, the shape, charge and volume of all molecular species in the system and the presence of ion currents. In particular, it describes the non-equilibrium organization of the polyelectrolyte layer and ion concentrations due to the presence of ion fluxes in the system.

Calculation results are presented for a short cylindrical nanopore with inner walls modified by an end-grafted polyelectrolyte layer. Ion current flows through this system upon applying a potential between the electrodes located in the reservoirs. In the very low applied potential regime, where the distribution of polyelectrolyte and ions is similar to that in equilibrium, a simple analytical model accounts for the conductance in excellent agreement with the calculations of the full non-equilibrium molecular theory. On the other hand, for a large applied potential bias the theory predicts a dramatic reorganization of the polyelectrolyte chains and the ions. This reorganization leads to non-linear (non-ohmic) current-potential curves. Moreover, it is shown that the morphology of the polyelectrolyte layer can be controlled by the direction and magnitude of the ion-fluxes.

The theory was also applied to model a neutral bare pore with outer walls modified by polyelectrolyte end-grafted layers of opposite charge. This system rectifies ionic currents: the conductivity when the positively charged polyelectrolytes face the negatively charged electrode (onstate) is larger than when them face the positively charged electrode (off-state). Ionic rectification is a desired property of nanopores and nanochannels as it enables applications in sensing and energy transduction. Our work shows that current rectification can be achieved in short neutral cylindrical nanopores by modification of the outer walls; this strategy is appealing for experiments since the outer walls can be chemically modified before drilling the pore. The effect of the pore dimensions and charge density of the outer walls on current rectification were analyzed. An analytical model was introduced that predicts the current-potential curves in excellent agreement with the non-equilibrium molecular theory calculations.
Aqueous Solutions of Atactic Poly (Methacrylic Acid) Studied at Various Degrees of Neutralization. Effect of NaCl Concentration.

Sitar Simona (1) , Aseyev Vladimir (2) , Kogej Ksenija (1)

(1) Department of Physical Chemistry, University of Ljubljana, Faculty of Chemistry and Chemical Technology, Ljubljana, Slovenia
(2) Department of Chemistry, Laboratory of Polymer Chemistry, University of Helsinki, Helsinki, Finland

Poly(methacrylic acid), PMA, is one of the most extensively investigated synthetic polyelectrolytes, mainly due to the conformational transition, which occurs in aqueous solutions when the carboxyl groups on the PMA chain are ionized.[1],[2] In aqueous solutions, PMA chain can either be in a compact or in an extended conformation, depending on the solution pH, i.e. on the degree of ionization of the carboxyl groups on PMA, and also on the ionic strength.

In the present work the dynamic and static light scattering measurements were performed on aqueous solutions of aPMA. Our aim was to study the effect of the degree of neutralization, \( \alpha_N \), and salt concentration, \( c_s \), on the polymer. We determined the radius of gyration, \( R_g \), the hydrodynamic radius, \( R_h \), and the shape parameter, \( \rho = R_g/R_h \), from which the conformation of scattering particles can be estimated. The polymer concentration was kept constant at 2 g/l. The concentration of salt, NaCl, was varied from 0.01 to 0.5 M, whereas \( \alpha_N \) varied from 0 to 1.

At \( \alpha_N = 0 \) for all salt concentrations, the correlation functions were bi-exponential. The corresponding relaxation times, \( \tau \), were associated with individual aPMA chains (small particles) and intermolecular associates (large particles). Hydrodynamic radii of the small particles were \( R_h,1 = (11-13) \) nm; no angular dependency of scattered light was obtained in this case. Hydrodynamic radii of the large particles, \( R_h,2 \), were in the range from 100 nm to more than 300 nm, depending on \( c_s \). The corresponding \( R_g,2 \), values for the large particles were obtained from the angular dependencies of the scattered light intensity. The calculated values of the shape parameter \( \rho \) were between 0.6 and 0.8 and were characteristic for microgels.[3]

Correlation functions obtained at \( \alpha_N > 0 \) were single exponential or bi-exponential, depending on \( c_s \). Given that at \( \alpha_N > 0 \) carboxyl groups on the aPMA chain are partly or completely neutralized and intermolecular association is suppressed, the reason for bimodal distribution in this \( \alpha_N \) range is so called polyelectrolyte effect.[4],[5] For high enough salt concentrations only one particle size was observed, which can be attributed to single aPMA chains. Their size increases from around 13 nm at \( \alpha_N = 0 \) to around (17-20) nm at \( \alpha_N \geq 0.5 \). Somewhat higher \( R_h \) values are consistent with chain expansion.

Complexation of Amphoteric Cryogels With Transition Metal Ions

Kudaibergenov Sarkyt (1) (2), Chopabayeva Nazira (1), Musayev Zhandos (3), Bekturov Esen (3)

(1) Laboratory of Engineering Profile, Kazakh National Technical University, Almaty, Kazakhstan
(2) Polymer Chemistry, Institute of Polymer Materials and Technology, Almaty, Kazakhstan
(3) Institute of Magistracy and PhD Doctoral Candidacy, Kazakh National Pedagogical University, Almaty, Kazakhstan

A series of macroporous amphoteric cryogels based on allylamine, methacrylic acid and acrylamide were involved into complexation reaction with transition metal ions. In our experiments sorption of metal ions in dynamic conditions was carried out by passing of 1 L aqueous solution of metal ions with concentration of 5 mg/L through cylindric amphoteric cryogels (d = 0.5 cm, l = 1.5 cm) with the flowing rate of 1.4–3.7 mL/min. In the course of passing of aqueous solution of metal ions through cryogel sample gradually colorization and shrinking of sample was observed. This is due to formation of coordination and ionic bonds with amine and carboxylic groups of cryogels respectively. The dynamic sorption capacity of amphoteric cryogels with respect to copper, nickel and cobalt ions was calculated. The amount of adsorbed metal ions varied from 99.17 to 99.55%. Dynamic exchange capacity of cryogels was in the range of 350–400 mg/L. Desorption of metal ions from cryogel volume was provided by disodium salt of ethylenediaminetetraacetic acid. The extracted amount of metal ions was equal to 75–80%. Figure demonstrates the adsorption and desorption curves of copper ions by amphoteric cryogel.

Fig. Sorption (a) and desorption (b) curves of copper ions by amphoteric cryogel.
The following advantages of amphoteric macroporous cryogels with respect to metal ions are outlined: 1) adsorption of metal ions can be provided in static and dynamic regimes; 2) adsorption and desorption process is simple, e.g. metal containing aqueous solution or desorbing agent is passed through the sample with definite rate; 3) high adsorption capacity of cryogels is due to presence of complex-forming ligands (amine and carboxylic groups) and high developed inner and outer surface; 4) the trace amount of metal ions may be concentrated up to 3 orders; 5) immobilized within macropores metal ions can easily be reduced by reducing agents and afterwards cryogels might be used as flowing catalytic microreactor.

Loosli Frédéric (1), Le Coustumer Philippe (2) (3), Stoll Serge (1)

(1) Environmental Physical Chemistry, Institut F.-A. Forel, University of Geneva, Switzerland
(2) Géoressources & Environnement, Université Bordeaux 3, France
(3) UFR STM, Université Bordeaux 1, France

The behavior of manufactured TiO2 nanoparticles is studied in a systematic way in presence of two natural polyelectrolytes, alginate and Suwannee River humic acids, at variable concentrations. TiO2 nanoparticles aggregation, disaggregation and stabilization are investigated using dynamic light scattering and electrophoretic experiments allowing the measurement of z-average hydrodynamic diameters and zeta potential values. At low monovalent salt concentration (NaCl 0.001M) stability of the TiO2 nanoparticles is discussed by considering three pH-dependent electrostatic scenarios. In the first electrostatic scenario, when pH is below the TiO2 nanoparticle point of zero charge, nanoparticles exhibit a positively charged surface whereas alginate and Suwannee River humic acids are negatively charged. Fast adsorption at the TiO2 nanoparticles occurs, promotes surface charge neutralization and aggregation. Charge neutralization (corresponding to the Iso Electric Point) is observed for a charge ratio of alginate over TiO2 equal to 1.25 and 1.40 for the humic acid over TiO2 ratio. By increasing further alginate and humic acids concentrations charge inversion and stabilization of TiO2 nanoparticles are obtained. In the second electrostatic scenario, at the surface charge neutralization pH, TiO2 nanoparticles are rapidly forming aggregates. Adsorption of alginate and Suwannee River humic acids on aggregates results in partial fragmentation. The kinetics of disaggregation are found greater in the case of alginate with an equilibrium time of approximately 45 min whereas the addition of SRHA requires one day before reaching size equilibrium. In the third electrostatic scenario, when nanoparticles, alginate and humic acids are negatively charged, only a small amount of humic acids is adsorbed on TiO2 nanoparticles surface owing to van der Waals interactions. TiO2 stability in presence of divalent and trivalent salts is also studied. It is shown that the presence of di and tri-valent salt is strongly modifying the interactions processes between the polyelectrolytes and TiO2 nanoparticles. Our study indicates that the fate and behavior of individual and aggregated TiO2 nanoparticles in presence of environmental polyelectrolytes (NOM) are mainly driven by the complex interplay between electrostatic attractive and repulsive interactions, steric effects and van der Waals interactions, as well as concentration ratio. Results also suggest that environmental aquatic concentration ranges of humic acids and biopolymers largely modify the stability of aggregated or dispersed TiO2 nanoparticles.
Charge and Mobility of Polyelectrolyte Complex Nanoparticles

Böhme Ute (1), Gelfert Karsten (1), Wiesner Brigitte (1), Lappan Uwe (1), Schwarz Simona (1), Scheler Ulrich (1)

(1) Polyelectrolytes and Dispersions, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

Polyelectrolyte complex nanoparticles formed from poly(maleicanhydride-coethylene) and poly(diallyldimethylammonium chloride) have been studied by a combination of NMR, EPR and light scattering under variation of the overall composition of the complexes. Dynamic light scattering and pulsed field gradient (PFG) NMR yield complementary information on the hydrodynamic size, where PFG NMR is more sensitive to primary complexes and DLS to the nanoparticles. The importance of primary particles for the total stability of the system has been shown. Electrophoresis NMR in conjunction with diffusion NMR permits the measurement of the effective charge of both the primary complexes and nanoparticles. By the NMR spectroscopic resolution the chemical species involved are identified in both diffusion and electrophoresis NMR. From the electrophoresis NMR data free polyelectrolytes are excluded all excess material, that is not incorporated in the nanoparticles is contained in primary complexes. Selective placements of spin labels on the polyanion permits the investigation of molecular dynamics by EPR lineshape analysis. showing strong reduction of the local mobility in the minority component. Comparative studies have been performed on dendrimers as monodisperse nanoparticles and on dendrimers with linear charged sidechains. These can mimic the expected corona structure on the polyelectrolyte complex nanoparticles. These sidechains exhibit significantly stronger counterion condensation compared to their linear counterparts.

References:
- Huber, K.; Scheler, U. New experiments for the quantification of counterion condensation Current Opinion in Colloid and Interface Science 17 (2012) 64-73
Folding And Aggregation Of Proteins In The Presence Of Amphiphilic Polyelectrolytes

Martin Nicolas(1), Ma Dewang (2), Winnik Françoise M. (2) (4), Herbet Amaury (3), Boquet Didier (3), Tribet Christophe (1)

(1) Department of Chemistry - UMR 8640 CNRS-ENS-UPMC, Ecole Normale Supérieure, Paris, France
(2) Department of Chemistry, Faculty of Pharmacy, Université de Montréal, Montreal, Canada
(3) Laboratoire d’Ingénierie des Anticorps pour la Santé, CEA Saclay, iBiTecS, SPI, France
(4) WPI International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, Japan

Biopharmaceutical protein products constitute the fastest growing class of human drugs. The development of these engineered proteins is yet hampered by their natural propensity towards irreversible aggregation particularly critical during refolding steps. A usual mean to prevent such aggregation relies on reversible immobilization (on chromatography columns), which limits the quantities that are manipulated, or on the addition of osmolytes (detergents, short polyols or ionizable amino acids) at high concentrations, which is costly and complicates in vivo injection or may bias in vitro tests. The use of polymers, and specifically of polyelectrolytes, may circumvent such limitations by combining features of both the immobilization and the osmolyte effects. Due to multipoint binding, including hydrophobic and coulombic reversible associations, macromolecules have significantly enhanced affinities for native proteins compared to small molecules and complex formation can prevent interprotein aggregation without significant perturbation of activity [1]. Non-toxic salt additives trigger in addition the release of proteins from polyelectrolyte complexes [2]. For these reasons, polyelectrolytes appear promising for improvement of refolding yields and it is of importance to study competitions between protein folding and protein:polymer association at intermediate refolding steps (while the hydrophobic residues are gradually buried into the protein and the charged hydrophilic ones are gathered at the protein’s surface).

We studied cytochrome c, a representative basic protein whose folding upon gradual crease of urea concentration is well documented, and antibody scFv fragments, as a model of complex proteins of high therapeutic value. To discriminate between the hydrophobic and coulombic contributions to protein:polymer interaction, we considered poly(acrylic acid) derivatives modified to contain a small fraction (<25mol%) of hydrophobic moieties. In situ variations of either charge density or hydrophobicity were obtained by introducing light-sensitive photo-ionizable hydroxylazobenzene groups or neutral azobenzene ones [3,4]. Circular dichroism and intrinsic fluorescence were used to characterize the protein folding. Fluorescence correlation spectroscopy and capillary electrophoresis were implemented to characterize the polymer:protein complexes along the refolding pathway.

In the case of scFv fragments, the efficient protection of polyanions at a weight ratio as low as 1:1 (i.e. typically at micromolar concentrations) was confirmed by native-like folding with no aggregation. Surprisingly, we found that the charge of the polyanions is of utmost importance in their interaction with the partially folded intermediates. The predominant contribution of coulombic interactions was confirmed by the disappearance of association at high ionic strength [5]. Electrostatic modeling of scFv surface showed positively-charged patches which may be responsible for the interaction with polyanions. Coulombic binding also appeared to be the predominant driving force that facilitate unfolding of cytochrome c in water/urea solutions. Upon exposure to light, photo-ionization was shown to affect the degree of unfolding, whereas photo-switch of the azobenzene with no ionization was ineffective at perturbing the protein, confirming that protein handling and control of folding can be achieved by playing with the coulombic interaction and photoionization of chromophores [6].

Hybrid inorganic-organic nanocomposites consisting of inorganic nanoparticles and functional polymers are novel and unique class of nanomaterials that synergistically combine and enhance the best properties of inorganic and organic polymers. They can be used as specialty coatings, sensors, biomaterials, membranes and sorbents for purification of drinking and sewage waters, selective extraction of different substances from industrial solutions, biological fluids and etc. Such nanoscaled sorbents due to their small size and very high specific surface area in comparison with traditional millimeter scaled sorbents possesses a set of improved physical and chemical, sorption and kinetic characteristics.

We have synthesized nano- and microscaled sorbents by interaction of TiO₂ nanoparticles with cationic polyelectrolyte – polyethyleneimine (PEI). The interaction was carried out by mixing of aqueous solutions of PEI and TiO₂ during 1 hour at room temperature. It was shown that the complexation of reacting components leads to formation of nonstoichiometric interpolyelectrolyte complexes (NPEC) enriched by TiO₂ nanoparticles. The composition of NPEC determined from the inflection points of potentiometric and conductimetric titration curves was equal to [TiO₂]:[PEI]=40:1 mol/mol.

Nanosorbents were characterized by XRD, DSC, SEM and IR-spectroscopy. According to SEM data the average size of TiO₂ particles was in range of 100-150 nm. Due to interaction of PEI macromolecules with negatively charged surface of TiO₂ particles the size of hybrid nanocomposites considerably increased and became 500-1500 nm.

The appearance of (1634 sm⁻¹) and νС–N (1220-1020 sm⁻¹) in FTIR spectrum of modified by PEI titanium dioxide confirmed the existence of amino groups in nanocomposite structure.

Nanoscaled sorbents were used for sorption of copper ions from aqueous solution. Experiments were carried out in static conditions by adding of 0.5 g of sorbent to 50 mL of solution. Adsorption results showed that Cu (II) removal efficiency by the nanocomposite increased with an increase of metal ions concentration in solution (Fig.).

![Fig. Sorption capacity (a) and removal efficiency (b) of copper ions by PEI/TiO2 nanocomposites in dependence of metal ions concentration in solution.](image)

Sorption capacity (SC) of nanosorbents increases from 0,45 to 5,0 mg/g upon changing of metal content from 1,7 to 20,7 mg/L. Dependence of removal efficiency (R) on metal ions concentration has extremal character. The biggest R value reached up to 65% at CCu 3,8 mg/L and gradually decreased with increasing of metal content in solution. Thus it is concluded that PEI/TiO₂nanocomposites are effective sorbents for removal of metal ions from aqueous solution.
Preparation, Characterization and Sorption Ability of Molecularly Imprinted Polymers

Kabdrakhmanova Sana(1), Battalova Ainur (1)

(1) NATIONAL SCIENTIFIC LABORATORY, Sarsen Amanzholy East Kazakhstan State University, Ust-Kamenogorsk, East Kazakhstan region, Kazakhstan

Molecularly imprinted polymers (MIPs) specifically "tuned" to target substances, in particular to metal ions, are important for determination, concentration and recovery of metal ions. The MIPs were prepared by in situ polymerization and crosslinking of acrylamide (AAm) and acrylic acid (AAc) within of which disodium salt of ethylenediaminetetraacetic acid (EDTA) was immobilized. The sorption capacity (SC), removal efficiency (RE) and distribution coefficient (DC) of MIPs with respect to metal ions were evaluated (Table).

The morphology of the MIP containing EDTA-Cu2+ complex is characterized by a macroporous structure where the content of copper is 17.55% (Figure).

The influence of pH medium, ionic strength and mixture of water-organic solvents on the behavior of MIPs was studied. All MIP samples exhibit maximal swelling at pH 6.0 and collapse in alkaline medium. The swelling ability of MIPs decreases with increasing of the ionic strength of the solution and volume fraction of organic solvent. Independently on the concentration of EDTA (from 10^-3 to 10^-1 mol/L) within AAm-AAc hydrogel matrix the shrinking degree and sorption capacity of MIPs with respect to metal ions is changed in the following order Pb+2>Cu+2>Zn+2.
Odd-Even-Effects In Polyelectrolyte Multilayers On A Quaternized Microgel Template

Gelissen Arjan (1), Schmid Andreas (1), Richtering Walter (1)

(1) Institute for Physical Chemistry, RWTH Aachen University, Aachen, Germany

Microgels are soft, cross-linked polymer networks with unique properties. Their stimuli-responsive ‘smart’ behaviour resulted in many publications using microgels for drug delivery, design of biomaterials, and in the development of sensors. Microgels show a huge potential in different fields of science and technology [1]. Charged microgels interact with linear polyelectrolytes [2,3]. These interactions are electrostatically and entropically [4] driven and result in particles containing negative and positive charges within the ensemble. This results in interesting amphoteric systems where multiple interactions can act in parallel with or against each other.

Polyelectrolytes can either penetrate microgels (polyelectrolyte absorption) or coat the microgel surface (polyelectrolyte adsorption). Polyelectrolyte adsorption is investigated with a positively charged microgel and long chain polyelectrolytes of PSS and PDADMAC, respectively. Quaternized microgels are a perfect template for layer by layer assemblies. The quaternized microgels are colloidally stable and because of their permanent charge, these microgels are pH independent.

Coating these charged microgels with polyelectrolytes influences the microgels size and electrophoretic mobility. The electrophoretic mobility reveals charge reversal after each layer deposition, clearly indicating polyelectrolyte adsorption at the microgel surface. The hydrodynamic radius decreases upon adsorption of the first layer and increases upon adsorption of the second layer. These experiments confirm the observations starting from an anionic microgel as described in [3]. The odd-even-effect is observed the first time for polyelectrolyte multilayers on a cationic microgel. These inverse experiments demonstrate that the odd-even-effect does not depend on the surface activity of the terminated layer. Both PDADMAC and PSS can induce shrinking and re-swelling of the microgel network and electrostatics play a decisive role.

Nonstoichiometric Polyelectrolyte Complexes Vs Polyanions as Templates on Caco3-Based Composites Synthesis

Mihai Marcela (1), Schwarz Simona (2), Simon Frank (3)

(1) Laboratory of Functional Polymers, "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania
(2) Polyelectrolytes and Dispersions Department, Leibniz-Institut für Polymerforschung Dresden e. V., Dresden, Germany
(3) Polymer Interfaces Department, Leibniz-Institut für Polymerforschung Dresden e. V., Dresden, Germany

The characteristics of calcium carbonate microparticles formed in supersaturated aqueous solutions, in the presence of some strong/weak anionic polymers or with nonstoichiometric polyelectrolyte complexes with negative charges in excess (NPEC-n), have been investigated under different relative inorganic/polymer ratio, tuned by initial solution supersaturation and polymer concentration. For this purpose two polyanions which contain the carboxylic and sulfonic ionic groups, poly(2-acrylamido-2-methylpropanesulfonic acid-co-acrylic acid) and chondroitin-4-sulfate, were used. NPEC-n dispersions prepared with the same polyanions and chitosan as polycation, were also used as templates for calcium carbonate crystallization. Scanning electron microscopy (SEM) was used to provide the particles morphology, and flow particle image analysis (FPIA) to evidence their mean size and sphericity. The polymer presence into the composite particles was evidenced by X-ray photoelectron spectroscopy (XPS), particles charge density and zeta-potential. The microparticles charge densities and their zeta-potential values suggested the uniform embedment of NPEC-n in the composites, irrespective of molar ratio, size and charge density of NPEC-n.
Study On Calcium Carbonate Microparticles Growth Template By A Double Hydrophilic Copolymer, Controlled By Inorganic/Polymer Ratio

Mihai Marcela (1), Mountrichas Grigoris (2), Pispas Stergios (2)

(1) Laboratory of Functional Polymers, "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania
(2) Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

The crystallization characteristics of calcium carbonate microparticles from supersaturated aqueous solutions in the presence of a double hydrophilic block copolymer poly(p-hydroxystyrene – b – methacrylic acid), PHOS-b-PMAA, have been investigated. The studies aim to highlight both the possibilities and the limitations of CaCO3/PHOS-b-PMAA microparticles formation under different relative inorganic/polymer ratio conditions, varying the initial solution supersaturation or the polymer concentration. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to provide high resolution of the particles morphology, whereas X-ray diffraction was used to determine the polymorphs type and crystallites characteristics. The polymer presence into the composite particles was evidenced by thermogravimetric analysis (TGA), particles charge density and zeta potential. The polymer induced sensitivity at environmental pH variations of the new composites, has been followed by streaming potential variation.
Synthesis and Characterization of New Hollow Calcium Carbonate/Polyanion Microspheres

Mihai Marcela (1), Doroftei Florica (1), Simionescu Bogdan C. (1) (2)

(1) Laboratory of Functional Polymers, "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania
(2) Department of Natural and Synthetic Polymers, "Gh. Asachi" Technical University, Iasi, Romania

The formation of hollow shells of calcium carbonate, by the principle of controlled nucleation and growth on a polyanion substrate, is discussed in this paper. To initiate the nucleation mechanism, which required the presence of calcium-binding acidic groups, a strong/weak anionic copolymer, poly(2-acrylamido-2-methylpropanesulfonic acid-co-acrylic acid), was used. The influence of polyanion concentration on the CaCO3 hollow microparticles growth from supersaturate aqueous solutions, at pH = 10.5 and after 8 h crystallization time, has been followed. The products were characterized by scanning electron microscopy, laser diffraction, X-ray powder diffraction, X-ray photoelectron spectroscopy, particle charge density, and zeta potential. In the presence of the copolymer, hollow-structured spherical particles, with medium sizes of 4 – 6 μm and containing just calcite polymorph, were obtained. The small increase of particles charge density, comparative with blank sample, showed that the polymer is located mainly inside the hollow particles and the calcite crystals on their surface.
Monte Carlo Simulations of Charged Nanogel Particles -- a Bead-Spring Model of a Polyelectrolyte Network

Bogdanovski Dimitri (1), Schneider Stefanie (1)

(1) Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

Charged nano- or microgel particles are solvent swollen, spherical polymer networks with sizes of 10 nm to 1 micrometer. The amount of solvent which is absorbed depends on the properties of the surrounding solution. They respond to changes in their environment by a change of their size. Therefore, these materials are often referred to as smart gels. One main advantage of the microgels, compared to macroscopic particles of the same material, is their fast response to external stimuli. For all charged polymer networks, the main driving force for the swelling is the entropy gain of the counterions which are electrostatically confined to the gel.

For macroscopic gels it is valid to assume that the number of counterions inside the gel is equal to the number of network charges and that surface effects can be neglected. Therefore, in a simulation model for a macroscopic gel, a simulation cell containing only a small part of the polymer network and periodic boundary conditions can be used. The number of positive and negative charges inside the gel has to be equal to ensure electro-neutrality.

In a nanogel however, surface effects can no longer be neglected and the complete gel particle has to be included in the simulation. Counterions are allowed to leave the gel and the gel particle is no longer electro-neutral. The ion distribution and the effective charge of the particle are important for two reasons. One reason is that the swelling of the particle is dependent on the number and the distribution of counterions inside the gel. The second reason is the influence of the effective charge and the electrostatic potential on the inter-particle interactions and on the stability of the colloidal suspension.

To calculate the ion distribution inside and around such a nanogel particle, we developed a model within the framework of the primitive model for electrolytes. The polymer particle was modeled as bead spring network of charged beads. The topology was chosen to be diamond-like, similar to the model of macroscopic polyelectrolyte gels developed by the author in previous work. [1] Gel radius, ion distributions and effective particle charges have been calculated for different charge densities, different particle concentrations, different counterion valence, and different salt concentrations. Furthermore, the distribution of the charges inside the gel was found to be important for the effective charge of the particle. In experimental systems, the charge distribution which highly depends on the preparation conditions (reaction rates of the co-monomers), is difficult to determine, and often not known. On the other hand, inhomogeneous charge distributions can be voluntarily achieved when core-shell particles are synthesized. Knowing the relation of the molecular structure, the resulting ion distribution, and the macroscopic swelling behavior will facilitate the design of tailor made nanogel particles.

Electrospinning Polyelectrolyte Complex: PH Responsive Fibers

Boas Mor (1), Gradys Arkadiush (2), Zussman Eyal (2)

(1) Russel Berrie Nanotechnology Institute, Technion, Israel
(2) Mechanical engineering, Technion, Israel

Polyelectrolytes are good candidates as active polymers. Thin multilayers of Polyelectrolytes complex demonstrate isotropic switching properties in response to pH external stimuli. Example to such complex is PAA (poly acrylic acid) and PAH (poly allylamine hydrochloride). Switchable properties are achievable due to switchable intermolecular interactions – shifting from ionic interactions to hydrogen bonds depending on surrounding. We propose to enhance interactions between those polyelectrolytes by fabricating quasi 1D nanofibers using electrospinning. Electrospinning is a kinetic process in which fibers comprising aligned and highly confined chains are formed under high electric field. It is assumed that this chains’ packaging will enhance intermolecular interactions along the fibers axis, resulting in enhancement of anisotropic physical properties of the responsive fibers. Polymer solution of 1:1 PAA/PAH was successfully electrospun resulting in fibers with diameters ranging from 300 to 800nm. Differential scanning calorimetry analysis of the fibers showed complete miscibility of the polymers. Anisotropic swelling of 600% increase in fiber diameter was observed when shifting from neutral to acidic aqueous surrounding. Electrospun responsive fibers can be implemented into various biological and industrial systems due to their high sensitivity and unique structure.
Conformation of a Natural Polyelectrolyte in Semidilute Solutions with No Added Salt

Josef Elinor (1), Bianco-Peled Havazelet (1)

(1) Chemical Engineering, Technion, Israel

We present a comprehensive study of the conformation of a model polyelectrolyte, alginate, in solutions with no added salt. We analyzed the full q dependence of small angle x-ray scattering (SAXS) plots and proposed a new model that has not been fitted to experimental scattering from polyelectrolytes yet. This model accommodates both the conformation of a chain and the electrostatic interactions between chains. Three models were examined as a way to represent the scattering from a single chain: a model of a worm-like chain, a model of a semiflexible chain without excluded volume effects, and a model of a semiflexible chain with excluded volume effects. The electrostatic interactions between chains were accounted for by using two models. We found that incorporating a Gaussian function to the model of the polymer reference interaction site (PRISM) has led to a good description of the experimental data.

Modeling the complete scattering curve allowed us to deduce information which was not available before for alginate. In particular, we found that the persistence length is not correlated with the chemical composition of the alginate. However, the electrostatic correlation length increases with the G-content. The dependence of the persistence length on the concentration was found to comply with the Odjik-Skolnick-Fixman (OSF) theory, where the persistence lengths depends on the square of the debye length. This new model has a potential to describe the scattering from other polysaccharides or polyelectrolytes.

A cross-over concentration from a string-controlled region to a bead controlled one was found in SAXS. Several rheological parameters have also changed abruptly around the same concentration.
Elastic Properties of Fluid Charged Membranes - a Coarse Grained Molecular Simulation Study

Avital Yotam Y. (1), Farago Oded (1)

(1) Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Be’er Sheva, Israel

Charged membranes and their interactions with the ionic solution surrounding them, have been the subject for study for many years. Specifically, it has not been fully understood how the membranes elastic properties are affected by the charge distribution. Here, we use coarse-grained (CG) molecular simulations to measure the bending rigidity and other elastic properties of bilayer membranes. Our particle-based model, that also accounts for the membrane thermal undulations, leads to new insights that are not captured by continuum models.
The Double-layer of Penetrable Ions: an Alternative Route to Charge Reversal

Frydel Derek (1), Levin Yan (2)

(1) Theoretical Chemical Physics Laboratory, ESPCI ParisTech, Paris, France
(2) Institute of Physics, The Federal University of Rio Grande do Sul, Porto Alegre, Brazil

We investigate a double-layer of penetrable ions near a charged wall. We find a new mechanism for charge reversal that occurs in the weak-coupling regime and, accordingly, the system is suitable for the mean-field analysis. The penetrability is achieved by smearing-out the ionic charge inside a sphere, so there is no need to introduce non-electrostatic forces and the system in the low coupling limit can be described by a modified version of the Poisson-Boltzmann equation. The predictions of the theory are compared with the Monte Carlo simulations.
Protein Self-Assembly of Anisotropic Monoclonal Antibody Equilibrium Clustering

Arzensek Dejan (1) (2)(3), Kuzman Drago (2), Podgornik Rudolf (3) (4)

(1) Netica, d.o.o., Slovenia
(2) Sandoz Biopharmaceuticals Menges, Lek Pharmaceuticals d.d., Slovenia
(3) Department of Physics, Faculty of Mathematics and Physics, Slovenia
(4) Department of Theoretical Physics, J. Stefan Institute, Slovenia

Stabilizing native globular proteins at high concentration is of broad interest in drug industry. Although concentrated proteins tend to develop high viscosities, aggregate and gel, which make their preparation very difficult, yet concentrated solutions of native proteins are possible. They can be crowded within clusters and kept in compact native form against unfolding where they self-assemble into equilibrium clusters without a problem [1]. The simplest physical description of globular proteins, such as monoclonal antibodies (mAbs), is through an analogy with colloidal particles and concepts from polyelectrolyte physics. Therefore, insight into dense equilibrium clusters of proteins, that could reversibly dissociate into monomers upon dilution, could be gained through electrostatically-driven clustering (aggregation) mediated by attractive interactions between oppositely charged local surface charge residues and short-ranged attractions like in depleted colloids near the isoelectric point [2]. Monoclonal antibodies (mAbs) are intrinsically complicated due to their heterogeneous surface composition originating from the polymeric character of the protein or due to the possibility of protein unfolding [3]. This implies non-isotropic interaction potentials arising from protein unique shape anisotropy, hydrophobic interactions, hydrogen bonds, salt specificity, but is most closely connected with the electrostatic surface charge distribution. They will prove vital for understanding how protein concentration modifies native-state stability and affects the self-assembly behavior. In the case of mAbs the surface charge distribution is highly inhomogeneous in terms of the charge residues on the protein surface, as well as their state of dissociation. This inhomogeneous charge distribution can lead to specific translational attraction or repulsion, affecting also the relative rotation of a protein with respect to another upon their approach [4]. To study these events, we quantified intermolecular interactions and liquid-liquid phase behavior to investigate the role of heterogeneous charge distribution on self-assembly. A protein model is proposed that takes into account the anisotropy of protein interactions that can describe the mAbs equilibrium thermodynamic behavior, protein-protein interactions, and basic aspects of the single-protein folding stabilization.


Lipid-Protein structure and interaction in inspired Myelin sheaths

Shaharabani Rona (1), Beck Roy (1)

(1) School of Chemistry, The Center for Nanoscience and Nanotechnology, School of Physics and Astronomy, Tel Aviv University, Tel Aviv, Israel

The compact myelin sheath formed around nerve axons speeds up nerve conduction and also nurtures the axon. Destruction of this sheath in demyelinating diseases such as multiple sclerosis (MS) results in nerve conduction failure and neurodegeneration. Myelin basic protein (MBP) is the second most abundant protein in the central nerve system (CNS), representing about 30% of the total myelin protein and about 10% of myelin by weight [1].

The sheaths are composed of multilamellar stacks of lipid-rich membranes which surround individual axons and account functionally for fast nerve conduction in thin fibers[2]. MBP binds to negatively-charged lipids on the cytosolic surfaces of the myelin membranes and is responsible for adhesion of these surfaces to form the roulade myelin structure in the CNS.

The unusual structural characteristics and functional requirements of the myelin sheath raise a number of pertinent biochemical questions concerning (1) the properties of the various lipid and protein components and their impact on the overall myelin morphology; (2) the precise molecular architecture of the membrane as dictated by protein-lipid, protein-protein, and lipid-lipid interactions; and (3) the connection, if any, between the lipid/protein components and the destruction of myelin in pathological situations such as MS[3].

In this study structural information are measured on length scales ranging from sub-nanometers to some tens of nanometers, under controlled buffer and temperature conditions. The studies are carried out with SAXS/WAXS techniques, which allow us to perform measurements on structures in the 0.1-100 nm range. Our preliminary results show massive structural difference between the healthy and the diseased lipid compositions models. With the addition of MBP to the lipid cytosolic system we clearly see a compaction of the system form around 120Å to 90Å and different MBP uptake in between the membrane. These results pave the way for better understanding the interactions responsible for the formation of the myelin sheaths and their dysfunction at diseased state.

Structure and Functionality of Charged Intrinsically Disordered C-terminal Tails of Neural Intermediate Filaments in Solution

Pregent Stive (1), Kornreich Micha (1), Malka-Gibor Eti (1), Lichtenstein Amir (1), Reiss Yuval (1), Laser-Azogui Adi (1), Patolsky Fernando (1), Beck Roy (1)

(1) The Center for Nanoscience and Nanotechnology, Tel Aviv University, Tel Aviv, Israel

Understanding the nature of interactions between biological molecules enabling the assembly of supramolecular structures is a central goal in biophysics. These structures are critical for a wide range of cellular functions, e.g. remodelling of the supramolecular structure of cytoskeletal proteins complexes, which occurs during cell division, locomotion, intracellular trafficking and signal transduction.

The cytoskeleton comprises three negatively charged proteins, including filamentous-actin, intermediate filaments and microtubules. The supramolecular assemblies of these cytoskeletal filaments are mediated, in vivo, by complex interactions between one or more types of cross-linking proteins and by unstructured regions radiating from the filament backbone.

The main objective of this study is to elucidate the nature of the structures and interactions in neurofilaments, the nervous system intermediate filaments. We aim to elucidate the dominant interactions between different C-terminus subunits intrinsically disordered highly charged tails once grafted to controllable surfaces and at various conditions to achieve new, highly functional, highly “tunable” bio-inspired materials and surface modifiers.

We acknowledge the support of Tel-Aviv University Nano-Center, the Israeli Science Foundation (Individual Research Grant 571/11), the European Community’s 7th Framework Programme (293402) and the Sackler Institute for Biophysics at Tel Aviv University.
Intermediate filaments (IFs) are one of three components of the cytoskeletal system, along with actin and microtubules. IFs are rather versatile: their expression patterns are cell- and tissue-type specific, providing each major cell type with a specific set of IF proteins specially designed to mechanically support its needs. The study of IFs interactions is key for understanding the IF network’s structure, stability and functions. In order to understand the way molecular alterations in the different IF proteins translates to designated supramolecular interactions, in our research we study neuronal IF protein structures and interactions. The main role recognized for neuronal IF is to increase the axonal caliber, thereby increasing nerve conduction velocity. Our study includes the three NFs subunit proteins (NF-L/NF-M/NF-H) and γ-internexin.

The IF hydrogel’s structures and interactions are examined using our in-house small angle X-ray scattering (SAXS) device and using 3rd generation synchrotron sources. The study of how supramolecular forces such as electrostatic, hydrophilic/phobic, and H-bonding are affecting on the above mentioned proteins and networks is achieved by tuning salt concentrations, pH, osmotic pressure, and temperature.
Dna Polyplexes Based On Cyclodextrin Polymers: Compaction And Endosomal Release

Amiel Catherine (1), Wintgens Veronique (1), Kichler Antoine (2)

(1) Chemistry, University Paris Est, Thiais, France
(2) Pharmacy, University of Strasbourg, Strasbourg, France

Complex macromolecular assemblies are realized from a combination of electrostatic and inclusion complex interactions. Ternary systems made of anionic polymer/ cationic surfactant/ β-cyclodextrin polymer have been elaborated in the frame of gene therapy with the need of new DNA vectors. The principle of the DNA vector is that a versatile “polycation” is formed by inclusion complexation between the β-cyclodextrin polymer and amphiphilic connectors which possess an adamantyl moiety and a cationic head group. We have studied the efficiency of several amphiphilic connectors on the DNA compaction process in order to evaluate the influence of the chemical structure, in terms of spacer and charge valency of the polar headgroup. The physico-chemical properties of the new vector have been correlated to their transfection abilities which have been successfully tested in vitro on several cell lines. In the absence of an endosomolytic agent, the transfection efficiency remains low because most of the complexes are trapped in the endosomal compartment. Here, we asked whether the addition of an imidazole modified adamantyl connector can increase the efficiency of the polyβCD/cationic adamantyl connector-based delivery system.
Enhanced Rigidity And Rupture Strength Of Composite Hydrogel Networks Of Bio-Inspired Block Copolymers

Rombouts Wolf Harald (1), Colomb-Delsuc Mathieu (2), Werten Marc (3), Otto Sybren (2), De Wolf Frits (3), Van Der Gucht Jasper (1)

(1) Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Wageningen, Netherlands
(2) Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands
(3) Wageningen UR Food & Biobased Research, Wageningen University, Wageningen, Netherlands

We study self-assembled composite networks consisting of silk-like protein fibers dispersed in a soft gel matrix formed by collagen-like block copolymers. Rheological analysis shows that the composite networks have significantly higher storage moduli than either of the single networks. This is caused by bundling of the fibrils due to depletion attraction induced by the collagen-like polymers. Moreover, the soft background network significantly modifies the non-linear response of the fibrillar network; the strain-hardening disappears almost completely and the stress and strain at which the gel breaks increase strongly, resulting in tougher hydrogels.
Liquid Crystals of Self-Assembled Bottle-Brushes

Storm Ingeborg (1), Leermakers Frans (1), Cohen Stuart Martien (1), de Vries Renko (1)

(1) Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Netherlands

The bottle-brush polymer architecture is very prominent in biology (proteoglycans, neurofilaments) and in current synthetic chemistry, but systematic comparison of theory and experiment for these molecules is hard in the absence of good model systems. We have previously shown that diblock polypeptides consisting of a long flexible hydrophilic block and a short positively charged binding block complex with semiflexible polyanions such as DNA to form self-assembled bottle-brush structures [1]. The self-assembled DNA bottle-brushes are a good model system for bottle-brushes since the length of the main chain polymer and grafting density can be easily tuned over a very wide range. Bottle-brush polymers are typically semiflexible and very thick, and may be expected to easily give rise to lyotropic liquid crystalline behavior. Despite well known biological examples of bottle-brushes with lyotropic liquid crystalline behavior (such as neurofilaments [2]), very little work has been done on the lyotropic liquid crystalline behavior of model bottle-brush polymers. Here we use our self-assembled DNA bottle-brushes to show that the bottle-brush coating pushes down the critical concentration for DNA liquid crystalline behavior to very low values, on the order of 1% in terms of DNA.

Specific Interactions of Cations with Polystyrenesulfonate in Dilute Solution and the Impact on the Phase Behaviour

Ezhova Anna (1), Huber Klaus (1), Hansch Markus (1)

(1) Physical Chemistry, University Paderborn, Paderborn, NRW, Germany

Anionic polyelectrolyte chains interact specifically with a number of metal cations in dilute solution. These interactions initially induce a collapse of the coils and cause a precipitation of the corresponding metal salt once a characteristic threshold is crossed. Two different types of thresholds could be identified. One threshold follows a phase boundary, which indicates a growing number of the metal cations required to precipitate the polyelectrolyte with increasing polyelectrolyte concentration and which thus corresponds to a stoichiometric amount of metal cations necessary to precipitate the respective amount of polyelectrolyte chains. This trend is called S-threshold.1 The second type of behavior, denoted as M-threshold, obeys the law of mass action, where the amount of metal cations necessary to precipitate the polyelectrolyte decreases with increasing concentration of polyelectrolyte.2 A particularly well investigated system in this field is anionic polyacrylates (PA) and the salts with various specifically interacting cations. Anionic PA chains exhibit an S-threshold with alkaline earth cations in dilute aqueous solution. Upon approaching this threshold, the PA chains collapse to compact particles, which start to aggregate once the threshold is crossed.3 Similar mechanistic details from other types of polyelectrolytes are still lacking as does the knowledge on the behavior of polyelectrolyte chains upon approaching and crossing the M-threshold. Also, the question whether anionic chains behave similar at an M-threshold (or an S-threshold), independent of its chemical nature is an entirely unsolved problem. It is these open questions, which shall be addressed in the investigation of polyelectrolytes in the presence of multivalent cations. To this end, experiments with polystyrenesulfonate (PSS) in 0.1 M NaCl-solution in the presence of Ba2+, Fe3+ and Al3+-ions were carried out in order to significantly broaden our knowledge on the phase behavior of polyelectrolytes with specifically interacting cations and morphological transformations induced close to the precipitation threshold. Care had been taken that the systems under consideration also include examples which exhibit an S-threshold.4 The experiments comprised simple turbidity measurements to establish phase diagrams as well as detailed light scattering close to the phase boundary in order to reveal structural information on single coils and aggregates at the respective boundary.

References

Modeling the Effect Of Adsorbed Polyelectrolytes on the Potential of Charged Particles for Electrophoretic Deposition Aspects

Rakita Yevgeny (1) (2) , Prof. Golodnitsky Dina (3) (4) , Dr. Natan Amir (5)

(1) Material Science and Engineering, Tel Aviv University, Tel Aviv, Israel
(2) Material and Interfaces, Weizmann Institute of Science, Rehovot, Israel
(3) School of Chemistry, Tel Aviv University, Tel Aviv, Israel
(4) Wolfson Applied Materials Research Center, Tel Aviv University, Tel Aviv, Israel
(5) Department of Physical Electronics, Tel Aviv University, Tel Aviv, Israel

The electrophoretic-deposition (EPD) method was tested in our electrochemistry research group to fabricate pristine and composite ceramic-polymer membranes for application in planar and 3D microbattery configurations. The goal of this work is to gain a phenomenological understanding of the EPD process for a system of charged colloidal particle covered with a polyelectrolyte (PE).

As a key factor for the different aspects of EPD (e.g. electrophoretic mobility, ion conductivity and particles interactions) is the electric potential, we developed a model for it on the basis of the Poisson-Boltzmann (PB) relation. To be close to experiment, the model addresses the physical parameters of the system used in our lab i.e. Yttria-Stabilized-Zirconia (YSZ) nanoparticles covered with polyethylenimine (PEI) as a dispersant in ethanol [1]. We simulate a set of scenarios in attempt to present the influence of the pH, surface potential, PE density, and the PE brush length on the electric potential and charge distribution profiles as a function of distance from the solid-surface/brush interface, where ‘brush’ is one of the possible PE configurations. Our results enabled us to draw conclusions on the effect of a PE additive on the suspension stability, as well as the morphology and electrokinetics of the electrophoretically deposited PE-stabilized particles.

In this work a fast and easy-to-operate simulator was derived, which enables flexibility in choosing any set of parameters that satisfies the model assumptions. Special algorithm was derived for PE brush with lengths smaller or comparable with the screening length. In addition, full analytical expression for the brush/bulk interfaces potential (Vs) and the Donnan potential (VD) were first presented in this study, which increases the accuracy of our model for a pH-dependent PE brush, unlike former studies [2]. The novelty of our model with respect of previously developed models [3, 4] is the combination of charged solid-surface (‘bare’ particle) with a charged brush-like PE layer (‘soft’ particle).


Complexation of Amphoteric Cryogels with Transition Metal Ions

Kudaibergenov Sarkyt (1) (2), Chopabayeva Nazira (1), Musayev Zhandos (3), Bekturov Esen (3)

(1) Laboratory of Engineering Profile, Kazakh National Technical University, Almaty, Kazakhstan
(2) Polymer Chemistry, Institute of Polymer Materials and Technology, Almaty, Kazakhstan
(3) Institute of Magistracy and PhD Doctoral Candidacy, Kazakh National Pedagogical University, Almaty, Kazakhstan

Complexation of amphoteric cryogels based on allylamine and methacrylic acid with transition metal ions was studied. The dynamic sorption capacity of amphoteric cryogels was determined. It was found that complexation of cryogels with transition metal ions is accompanied by coloring and shrinking of samples.
Modeling the Effect of Adsorbed Polyelectrolytes on the Potential at Charged Surfaces for Electrophoretic Deposition Aspects

Rakita Yevgeny (1) (2) , Prof. Golodnitsky Dina(3) , Dr. Natan Amir

(1) Material Science and Engineering, Tel Aviv University, Tel Aviv, Israel
(2) Material and Interfaces, Weizmann Institute of Science, Rehovot, Israel
(3) School of chemistry, Tel Aviv University, Tel Aviv, Israel

The electrophoretic-deposition (EPD) method was tested in our electrochemistry research group to fabricate pristine and composite ceramic−polymer membranes for application in planar and 3D microbattery configurations. The goal of this work is to gain a phenomenological understanding of the EPD process for a system of charged colloidal particle covered with a polyelectrolyte (PE).

As a key factor for the different aspects of EPD (e.g. electrophoretic mobility, ion conductivity and particles interactions) is the electric potential, we developed a model for it on the basis of the Poisson-Boltzmann (PB) relation. To be close to experiment, the model addresses the physical parameters of the system used in our lab i.e. Yttria-Stabilized-Zirconia (YSZ) nanoparticles covered with polyethylenimine (PEI) as a dispersant in ethanol [1]. We simulate a set of scenarios in attempt to present the influence of the pH, surface potential, PE density, and the PE brush length on the electric potential and charge distribution profiles as a function of distance from the solid-surface/brush interface, where ‘brush’ is one of the possible PE configurations. Our results enabled us to draw conclusions on the effect of a PE additive on the suspension stability, as well as the morphology and electrophoretics of the electrophoretically deposited PE-stabilized particles.

In this work a fast and easy-to-operate simulator was derived, which enables flexibility in choosing any set of parameters that satisfies the model assumptions. Special algorithm was derived for PE brush with lengths smaller or comparable with the screening length. In addition, full analytical expression for the brush/bulk interfaces potential (Vs) and the Donnan potential (VD) were first presented in this study, which increases the accuracy of our model for a pH-dependent PE brush, unlike former studies [2]. The novelty of our model with respect of previously developed models [3, 4] is the combination of charged solid-surface (‘bare’ particle) with a charged brush-like PE layer (‘soft’ particle).

Complexes of Charged Lipids and Oppositely Charged Polyelectrolytes Characterized by Cryo-TEM

Ronen Maor (1), Talmon Yeshayahu (1)

(1) Chemical engineering, Technion, Haifa, Israel

In recent years there has been rising interest in the study of the mechanisms governing the complexation of polyelectrolytes and oppositely charged lipids. This is due to their interesting and still not completely understood phenomenology, and more so to the increased awareness of their potential for innovative applications in nano-medicine and nano-biotechnology, as in gene-delivery.

In this work we used direct-imaging cryo-TEM to study the structural evolution on the nano-level, as the charge-ratio between a negative polyelectrolyte and a cationic lipid is changed. Charge ratio (CR) is the ratio between the negatively charged groups of the polymer and the positively charged groups of the lipids. This system was composed of reduced bis(11-ferrocenyldodecyl)-dimethylammonium bromide (BFDMA), a positively charged synthetic double-tailed cationic lipid and sodium poly(acrylic acid) (NaPAA), a negatively charged polyelectrolyte.

We observed different nanostructures with changing CR. First, solution of pure BFDMA (1 mM) had only polydispersed population of large unilamellar vesicles, 200 nm – 1 µm, in diameter. Upon addition of appropriate amount of PAA to the BFDMA solution to give varying values of CR, we saw formation of the multilamellar complexes. The unilamellar vesicles start to add on more layers of cationic lipid, where the polyelectrolyte is sandwiched in the middle screening the electrostatic repulsion. As CR approached unity, the structures tended to aggregate and form larger complexes, since each complex has a neutral charge, which allows them to get in close proximity. Once they are close, they are attracted to each other by short-range interactions. Beyond CR of 1, aggregated clusters are not seen, and the structure average size decreases. However, only at CR of 2 we observed structures that are facetted. At other CR > 1 values, round multilamellar liposomes were dominant structure in solution.

Another system under current investigation is the system of 1,2-dioleoyl-3-trimethylammonium-propane (DOTAP) and NaPAA. We would like to find out whether the trends described above hold in another type of cationic lipid.
Effect Of Counter-Ion Exchange Between Charged Macromolecules

Kim Won Kyu (1), Netz Roland R. (1)

(1) Physics, Free University Berlin, Berlin, Germany

We study the effect of the counter-ion exchange between charged macromolecules on their interactions and also on the dielectric response of the macromolecule solutions. We show, by scaling theory and Monte Carlo simulations, that the counter-ion exchange between macromolecules induces like-charge attraction, which have originated from monopole-monopole interactions, in the highly charged limit. Moreover, we find that the dynamical time scale of the counter-ion exchange in a polyelectrolyte (PE) solution is responsible for the dielectric response in so-called the super low frequency (SLF) regime, which was found and suggested in recent simulation work [S. Fischer and R. R. Netz, The European Physical Journal E, 36, 117 (2013)]. Our results show the effect of thermally activated barrier-hopping of counter-ions on the relaxation time of the SLF mode.
Specific Ion Binding to Amphiprotic Surface Groups and the pH Dependence of the Hofmeister Series

Schwierz Nadine (1), Netz Roland R. (2)

(1) Physics Department, Technical University Munich, Garching, Germany
(2) Physics Department, Freie Universität Berlin, Berlin, Germany

Ion specific effects are ubiquitous. The term denotes the fact that most aqueous physicochemical processes not only depend on ion concentration and valency, but also on the ion type. Anions and cations can be ordered reproducibly according to their efficiency to precipitate proteins from solution into the Hofmeister series. However, today state of the art experiments reveal a whole spectrum of direct, altered and reversed ordering calling the presumed universality of the series into question.

Ion binding to amphiprotic surface groups is one of the central mechanisms for ion-specificity if ionizable groups are present on the surface of a macromolecule. To gain insight into the microscopic mechanism, we use a combination of atomistic simulations and Poisson-Boltzmann theory and bridge from computational results to macroscopic experimentally accessible properties.

In our modeling approach, we first extract single-ion surface interaction potentials at atomistically resolved surfaces composed of uncharged carboxyl (COOH) groups and of charged carboxylate (COO-) groups. The surface affinity of single ions depends strongly on whether the carboxyl group is dissociated or not and is even reversed for cations.

Phase diagrams, based on long-ranged forces between two heterogeneous surfaces containing carboxyl and carboxylate groups interacting across electrolyte solutions, feature direct, reversed and altered Hofmeister series in dependence of the salt concentration and pH. The results provide a microscopic explanation for the pH dependence of the Hofmeister series due to specific and diverse ion binding to carboxyl and carboxylate surface groups.