

European Science Foundation
Standing Committee for Physical and Engineering Sciences (PESC)

ESF PESC EXPLORATORY WORKSHOP

Ch@ins: The Limits Of Neutrality



Compiègne, France, 14 - 17 September 2006

Convened by:

① Jean Dailant, ① Patrick Guenoun and ② Carlos Marques

① SCM, CEA Saclay

② ICS Strasbourg, CNRS

EXECUTIVE SUMMARY

The ESF Exploratory Workshop - EW05-160 "Chains : limit of neutrality" took place in Compiègne over three days and a half from September 14th, 2006 to September 17th, 2006. This meeting conveyed 28 people of 17 different nationalities in the Hotel "Au relais Napoléon" of Compiègne which presented a single place for all participants for lodging and meetings. As planned, this choice favored a lot informal discussions and contacts between participants in periods around meetings since they could meet easily in the lobby and the lodge close to the bar, even late at night. Meals were also taken at the same place, still strengthening contacts between people. This was particularly important for such a short meeting with a tight agenda but where important decisions had to be taken in order to extend the action started as depicted in conclusions.

Participants were chosen in purpose for their their personal accomplishments in the field but also because the convenors thought they could efficiently complement each other by bringing an original point of view on a subject, ion specificity, that all of them did not really tackle explicitly. As a consequence quite a number of participants were quite astonished to have been conveyed to such a meeting and, quite often, did not meet many of the others previously. We thought this was a very efficient melting which helped promoting original approaches, sometimes controversies, that the field needed.

As a matter of fact, this meeting was organized since ion specificity in physico-chemistry of short and long chains is a long standing ill-resolved problem. Lots of data have been generated by so far, mostly by macroscopic methods and a classification has emerged, the so-called Hofmeister series. Such series has never received any firm basis from microscopic models, except some recent but still controversial theoretical attempts. However, new experimental techniques are now at hand to supplement such theoretical efforts. In view of this timely perspective, the conveyors thought the situation was ripe enough to catalyze efforts with such a small-size, well-focused workshop which was then approved and granted by ESF.

The agenda was set-up by thematic sessions, concluded by a round-table each, before a general conclusive round-table on the last day morning. The first session was devoted to effects of stabilization, destabilization and crystallization under the influence of salts of various kinds. These effects are the most spectacular and led Hofmeister to propose his series by observing proteins salting-in and out. This session was then very helpful in order to recall basic facts and observations which are extremely useful in day to day life of people aiming at crystallizing proteins. In a sense this session provided the basic and common knowledge and language to participants for the rest of the meeting. In particular, definitions and classifications were deeply discussed during the following round-table.

The second session dealt with the peculiar case of lipids and surfactants where the self-assembly of these molecules depends on the nature of the added salt. Various geometries are relevant to this problem but the case of planar lipid membranes has been studied extensively, both experimentally and also by theories which are only semi-microscopic.

A third session was about polymers, where suprisingly, strong effects appear both for neutral and charged chains. In particular strong conformational changes, even like chain collapse, can be induced by salt addition. On Saturday two sessions took place and the place of theory and simulation was first debated. The real issue was clearly defined as being an adequate description of the solvent, quite often water which present a very anisotropic structure. This was an excellent introduction for the afternoon session which was devoted to charges and hydrogen bonds at surfaces. In particular it was recognized that the solvation of ions has to be carefully quantified in order to interpret neutron scattering data. Other microscopic techniques were also presented which now should provide a wealth of data for future crucial tests of theories.

Scientific content

Summary of presentations:

Stabilization, destabilization and crystallization

Werner Kunz Specific ion effects in polyelectrolyte and cationic surfactant systems

W. Kunz discussed in detail the activity coefficients of ions, concentration effects and the role of pH. He discussed the consequences of ion specificity for gas solubility and bubble coalescence, lipid self-assembly, complexation and specific crystallization of biomorphs.

Michael Gradzielski Ionic Block copolymer Micelles and their Interpolyelectrolyte Complexes -Structure and Dynamics

M. Gradzielski mainly discussed salt effect in ionic block copolymer micelles. He described small angle neutron scattering experiments, the response of micelles to stimulations and surface tension of solutions.

Madeleine Ries Ionic specificity in Protein Crystallisation : effect on molecular interactions, solubility, polymorphism and structure

M. Ries gave a detailed account of specific effects in protein crystallization. She described generic phase diagrams and possible reversal of Hofmeister series depending on the protein.

Pierandrea Lo Nostro Specific ion effects in biological systems

P. Lo Nostro described specific effects in lipidic systems and amino acids as revealed by viscosity, optical activity and surface tension measurements.

The need for more refined predictions in order to account for macroscopical observations was emphasized during the following round table.

Lipids, Surfactants and Salts.

Epameinondas Leontidis Specific ion effects in physicochemical and biological systems. Understanding them through simulations, experiments and theory in model systems

E. Leontidis addressed the following questions: Are ion specific effects really interfacial phenomena ? What is the role of the solvent? Are they local or collective effects? Why did we sometimes get irregular or inverted series? His discussion was illustrated using examples from the free surface of electrolyte solutions or monolayers and bilayers of zwitterionic lipids.

Volker Schädler Control of interactions and stability in polymer complexes - a dream?

V. Schädler discussed the control of interactions in polymer complexes with a special emphasis on polymer-polymer complexes like polyethylene oxide -polypropylene oxide and polyacrylic acid.

André Laschewsky Controlling the self-organization of poly(zwitterions) by the interaction with low molar mass salts: pathways toward advanced materials.

A. Laschewsky showed how the aggregation of poly-zwitterions could be controlled with salts, and how their efficiency follows the Hofmeister series. He also showed how responsive materials can be built with such polymers.

Horia Petrache Salt screening and specific ion adsorption determine neutral-lipid

membrane interactions

H. Petrache discussed a very interesting effect where the interaction between membranes is tuned by specific adsorption controlled screening.

Rumiana Dimova Ions interacting with membranes... and in-between comes water

R. Dimova discussed the interaction of ions, in particular Ca ions with membranes and how the elasticity and shape of membranes could be affected.

Neutral ... or not so neutral polymers.

Martien Cohen-Stuart The plusses and minuses of polymer self-assembly

M. Cohen-Stuart described how polymer self-assembly can lead to complex structures like core-shell ones by playing with coulombic and other interactions. His talk was based on beautiful neutron scattering and atomic force microscopy experiments.

José M.G. Martinho Association of hydrophobically modified poly(N,N-dimethylacrylamide) in water probed by fluorescence

J. Martinho showed how fluorescence could be used to investigate the association of polymers in water.

Lennart Picullel Cat-and anion specific effects on the coil-helix transition and further aggregation of kappa carrageenan

L. Picullel described the effect of ions of the reversible coil-to-helix transition in kappa carrageenan. This effect is apparently related to changes in the area exposed to solvent. Cation binding is apparently size selective but the nature of anion binding remains unclear.

S. Cremer Investigating polymer collapse on a chip

S. Cremer described very novel experiments of polymer collapse (PNIPAM) on microfluidics chips. This method allows a range of different concentration and temperature conditions to be explored in a single experiment and can be couple to IR spectroscopy.

Heikki Tenhu Temperature-sensitive properties of poly(N-isopropylacrylamide) mesoglobules formed in dilute solutions heated above their demixing point

H. Tenhu discussed the mesostructures in polymers like PNIPAM heated above their demixing point. He showed in particular that Li ions lead to larger, less stable mesoglobules.

The differences between Na and Li were emphasized in the following round table as well as the conformation of the chains and the role of phosphates for biological applications.

What can theory and simulations predict?

Luc Belloni Specific short-range ionic effects: from primitive model to discrete solvent levels of description

L. Belloni discussed theoretical descriptions of specific effects starting with the primitive model. He showed that because of (?) limited success in the description of specific effects, discrete molecular models of the solvent are needed.

Vojko Vlachy Ion-specific effects in polyelectrolyte solutions

V. Vlachy described ion specific effects in polyelectrolyte solutions. He concentrated in particular on thermodynamic properties which are ion specific.

Matthias Boström Why intermolecular forces follow Hofmeister sequences ?

M. Boström discussed in detail the role of dispersion forces on ion specificity.

Nico van der Vegt Modeling effective ion-ion interactions in aqueous solution

N. van der Vegt described in particular Monte-Carlo simulations. He argued that osmotic properties are insensitive to the details of the potential at least in the case of NaCl. A main conclusion of his talk was that polarizable water models are not necessary to get specific effects.

Alina Ciach Mesoscopic theory for highly charged colloids

A. Ciach described a density functional approach of highly charged colloids.

Most of the following round table was devoted to the discussion of water potentials and whether polarisable potentials were necessary to describe specific effects.

Charges and Hydrogen Bonds at surfaces

George Neilson Neutron and X-ray scattering studies of ionic structure in aqueous solutions.

G. Neilson described beautiful neutron scattering experiments using deuteration for the full determination of ionic structures in water.

Stefan Ulvenlund Effects of ion binding and inter-molecular hydrogen bonds on the arrangement of hydrophobic peptide helices at the air-water interface.

Implications for the physical stability of peptide solutions.

S. Ulvenlund described the organization of peptides on surfaces and how they can be tuned by using ions.

Alla Oleinikova Percolation transition of hydration water at the surface of macromolecules

A. Oleinikova described beautiful simulations of the percolation of hydrogen bonds at the surface of biological macromolecules. Fractal dimensions and lifetime of clusters could in particular be determined. The fractal dimension of the largest cluster is 1.896 and its lifetime about 1ps.

Lubos Vrbka Ion solvation at surfaces of hydrated proteins and other interfaces

L. Vrbka described impressive simulations of surface concentrations and binding of ions on proteins in solution. He showed that air-water and protein-water surfaces are very different in this respect. He also showed that chloride and sulphate bind independently.

Padmanabhan Viswanath Addressing ion specificity through grazing incidence x-ray fluorescence and sum frequency spectroscopy techniques

V. Padmanabhan showed very interesting complementary experiments. He used x-ray fluorescence to determine surface concentration of ions and sum-frequency generation spectroscopy to determine their water environment.

Assessment of the results, contribution to the future direction of the field, outcome :

At last, on Sunday morning, a conclusive round-table “Discussion across the borders, how to reconcile viewpoints, key experiments and simulations” tried to pave the way for the future of the field. In particular it appeared that larger scale collaborative instruments were needed in order to take benefits of the new theoretical and experimental approaches which have appeared, and also of comparing new data with the very large amount already collected. In that respect, re-analysis of old data and, sometimes some remakes would be very fruitful.

It was then decided by the participants that the convenors should take the initiative of a larger proposal in the framework of ESF in order to capitalize the assets of such a fruitful, though short, meeting. We then proposed the so-called SOSPECOF initiative for “Solvent mediated specific ionic effects in complex fluids” at the PESC committee of ESF for ESF Research networking programmes. Unfortunately this initiative was not approved.

Final program

Thursday, September 14th 2006

14:00 Welcome and Introduction

Afternoon Session: Stabilization, Destabilization and Crystallization.

14:30 *Keynote address:* Werner Kunz Specific ion effects in polyelectrolyte and cationic surfactant systems

15:30 Michael Gradzielski Ionic Block copolymer Micelles and their Interpolyelectrolyte Complexes -Structure and Dynamics

16:00 *Coffee Break*

16:30 Madeleine Ries Ionic specificity in Protein Crystallisation : effect on molecular interactions, solubility, polymorphism and structure

17:00 Pierandrea Lo Nostro Specific ion effects in biological systems

17:30 *Round Table lead by* Rumiana Dimova

Friday, September 15th 2006

Morning Session: Lipids, Surfactants and Salts.

08:30 *Keynote address:* Epameinondas Leontidis Specific ion effects in physicochemical and biological systems. Understanding them through simulations, experiments and theory in model systems

09:30 Volker Schädler Control of interactions and stability in polymer complexes - a dream?

10:00 André Laschewsky Controlling the self-organization of poly(zwitterions) by the interaction with low molar mass salts: pathways toward advanced materials.

10:30 *Coffee Break*

11:00 Horia Petrache Salt screening and specific ion adsorption determine neutral-lipid membrane interactions

11:30 Rumiana Dimova **Ions interacting with membranes... and in-between comes water**

12:00 *Round Table lead by* Carlos Marques

Afternoon Session: Neutral ... or not so neutral polymers.

14:00 *Keynote address:* Martien Cohen-Stuart The plusses and minuses of polymer self-assembly

15:00 José M.G. Martinho Association of hydrophobically modified poly(N,N-dimethylacrylamide) in water probed by fluorescence

15:30 Lennart Piculell Cat-and anion specific effects on the coil-helix transition and further aggregation of kappa carrageenan

16:00 *Coffee Break*

16:30 S. Cremer Investigating polymer collapse on a chip

17:00 Heikki Tenhu Temperature-sensitive properties of poly(N-isopropylacrylamide) mesoglobules formed in dilute solutions heated above their demixing point

17:30 *Round Table lead by* Patrick Guenoun

Saturday, September 16th 2006

Morning Session: What can theory and simulations predict?

08:30 *Keynote address:* Luc Belloni Specific short-range ionic effects: from primitive model to discrete solvent levels of description

09:30 Vojko Vlachy Ion-specific effects in polyelectrolyte solutions

10:00 Matthias Boström Why intermolecular forces follow Hofmeister sequences ?

10:30 *Coffee Break*

11:00 Nico van der Vegt Modeling effective ion-ion interactions in aqueous solution

11:30 Alina Ciach Mesoscopic theory for highly charged colloids

12:00 *Round Table lead by* Werner Kunz

Afternoon Session: Charges and Hydrogen Bonds at surfaces

14:00 *Keynote address:* George Neilson Neutron and X-ray scattering studies of ionic structure in aqueous solutions.

15:00 Stefan Ulvenlund Effects of ion binding and inter-molecular hydrogen bonds on the arrangement of hydrophobic peptide helices at the air-water interface. Implications for the physical stability of peptide solutions.

15:30 Alla Oleinikova Percolation transition of hydration water at the surface of macromolecules

16:00 *Coffee Break*

16:30 Lubos Vrbka Ion solvation at surfaces of hydrated proteins and other interfaces

17:00 Padmanabhan Viswanath Addressing ion specificity through grazing incidence x-ray fluorescence and sum frequency spectroscopy techniques

17:30 *Round Table lead by* Jean Daillant

Sunday, September 17th 2006

Morning Session: Discussion across the borders, how to reconcile distinct viewpoints, key experiments and simulations?

09:00 *Round Table lead by the five previous keynote speakers*

11:00 *Closing and farewell drink*

List of Participants

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Statistical information on participants

Total number of participants: 27 (excluding ESF Representative)

By country of residence (work):

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1 CZ	1 PT
7 DE	3 SE
1 FI	1 SI
6 FR	1 UK
1 IT	2 US
1 NL	

By gender:

24 Male

3 Female