Molecular Arrangement, Electronic Structure and Transport Properties in Surfactant Gel- and Related Systems Studied by Soft X-ray and Dielectric Spectroscopy

JOHAN GRÅSJÖ
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Abstract

This thesis concerns studies of aqueous soft matter systems, especially surfactant micelle systems.

The aim has been to study the molecular arrangement and electronic structure of the constituents of, as well as transport properties in such a system. The molecular arrangement and electronic structure has been studied by means of X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray spectroscopy (RIXS). The transport properties have been investigated by low-frequency dielectric spectroscopy (LFDS) and small angle X-ray scattering (SAXS) as well as a theoretical modelling. The latter was based on Fick’s laws of the release from binary surfactant system and was validated by experiments.

The RIXS and XAS measurements show the electronic structure in bulk water and the influence of the chemical surrounding of the water molecule in bulk water and of the water molecules confined in a micelle lattice. The spectra are highly dependent on the molecular arrangement in such systems. For glycine and sodium polyacrylate RIXS and XAS spectra show features which are unique for carboxyl and carboxylate groups and such measurements can thus be used for fingerprinting.

The LFDS and SAXS measurements show a strong correlation between structure in a surfactant/poly-ion system and apparent mobility of surfactants. This conclusion is in line with earlier observations.

By the theoretical modelling a predictive model for the surfactant release from a binary surfactant micelle system has been obtained and the importance of different factors for surfactant release has been further clarified.

Keywords: surfactants, surfactant/poly-ion gel, water, confined water, XAS, RIXS, dielectric spectroscopy, SAXS, pKa, transport, Fick’s law

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


IV Johan Gråsjö, Per Hansson and Maria Strømme: “Ion mobility and gel complex structure in dodecyltrimetylammonium/polyacrylate gel complexes” (manuscript)


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Comments on my contribution to the listed papers

I  I performed, jointly with co-authors, the soft x-ray spectroscopy measurements and participated in the preparation of the paper.

II I planned the experiments, prepared the samples, performed the pre-study regarding the relationship between relative humidity and water content in the sample, performed, jointly with co-authors, the soft x-ray spectroscopy measurements and contributed significantly in the preparation of the paper.

III I planned the experiments, prepared the samples, performed, jointly with co-authors, most of the soft X-ray spectroscopy measurements and contributed significantly in the preparation of the paper.

IV I planned the experiments, prepared the samples, performed the dielectric spectroscopy measurements and analyses and wrote the major part of the paper.

V I developed the fundamental equation for the article and wrote the major part of the paper.

VI I implemented the numerical calculation for surfactant release through a membrane and developed, jointly with co-authors, the transport equation for the release from a gel matrix and participated in the preparation of the paper.

VII I contributed to the development of the approximate solution of the transport equation for the release from a gel matrix (paper VI) and participated in the preparation of the paper.

Also published


Erik Sjögren, Hans Lennernäs, Tommy B. Andersson, Johan Gräsjö and Ulf Bredberg. “The multiple depletion curves method provides accurate estimates of intrinsic clearance, maximum velocity of the metabolic reaction (Vmax) and Michaelis constant (Km): Accuracy and robustness evaluated through experimental data and Monte Carlo simulations”, Drug metabolism and disposition, 37, No1, p. 47-58 (2009)


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<td>$A$</td>
<td>area of radiation source</td>
</tr>
<tr>
<td>$A_{mem}$</td>
<td>area of membrane</td>
</tr>
<tr>
<td>$a$</td>
<td>acceleration of charge</td>
</tr>
<tr>
<td>$B_{\Delta\omega}$</td>
<td>brilliance</td>
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<tr>
<td>$B_0$</td>
<td>magnetic field</td>
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<td>$C_i$</td>
<td>surfactant concentration</td>
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<td>$C_0$</td>
<td>capacitance</td>
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<td>light velocity</td>
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<td>Miller indices</td>
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<tr>
<td>$I$</td>
<td>intensity</td>
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<tr>
<td>$K$</td>
<td>$= e B_0 \lambda_u / 2 \pi m_e c$</td>
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<tr>
<td>$k$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$L_{el}, L_1, L_2$</td>
<td>electrode spacing</td>
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<tr>
<td>$L_D$</td>
<td>diffusion length</td>
</tr>
<tr>
<td>$m$</td>
<td>order of reflection</td>
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<tr>
<td>$m_e$</td>
<td>mass of electron</td>
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<tr>
<td>$N$</td>
<td>number of periods in an undulator</td>
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<tr>
<td>$n_0$</td>
<td>number of charge carriers</td>
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<td>$P$</td>
<td>radiation power</td>
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<tr>
<td>$Q$</td>
<td>charge</td>
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<tr>
<td>$R_{Row}$</td>
<td>radius of Rowland circle</td>
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<tr>
<td>$R$</td>
<td>molar gas constant</td>
</tr>
<tr>
<td>$S_i$</td>
<td>micelle-bound surfactant concentration</td>
</tr>
<tr>
<td>$s$</td>
<td>groove spacing</td>
</tr>
<tr>
<td>$T_{op}, T'_{op}$</td>
<td>dipole operator</td>
</tr>
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$T$ temperature
$t$ time
$V(x,y,z)$ electric potential
$V_{sol}$ volume of micelle solution
$W$ interaction energy
$w$ slit width
$X$ arbitrary real number
$x$ x-coordinate
$x_i$ mole fraction of surfactant in micelle
$Y^*$ admittance
$Z^*$ impedance
$\Delta z_{res}$ detector spatial resolution

$\alpha_i$ mole fraction of surfactant
$\beta$ interaction energy scaled by thermal energy
$\Gamma$ lifetime broadening
$\gamma$ the Lorentz factor
$\delta$ electrode spacing scaled by the diffusion length
$\varepsilon^*, \varepsilon', \varepsilon''$, complex relative permittivity, real part, imaginary part
$\varepsilon_0$ permittivity of free space
$\Theta_{rad}$ radiation angle relative the electron acceleration
$\theta_{inc}, \theta_{ex}$ incidence and exit angles
$\theta_{rad}$ radiation angle relative electron velocity
$\eta$ Boltzmann transformed distance
$\lambda$ wavelength
$\lambda_u$ undulator periodicity spacing
$\mu$ mobility
$\mu_{dip}$ dipole moment
$\sigma^*, \sigma', \sigma''$, complex conductivity, real part, imaginary part
$\tau$ relaxation time
$\Psi$ state wave function
$\psi$ one electron wave function
$\Omega$ solid angle
$\omega$ angular frequency
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>AD/DA</td>
<td>Analog to digital and digital to analog converters</td>
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<tr>
<td>CMC</td>
<td>Critical Micelle Concentration</td>
</tr>
<tr>
<td>DLVO-model</td>
<td>Derjaguin-Landau-Verwey-Overbeek-model</td>
</tr>
<tr>
<td>DoTA</td>
<td>Dodecyltrimethylammonium</td>
</tr>
<tr>
<td>DoTAB</td>
<td>Dodecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>DoTAC</td>
<td>Dodecyltrimethylammonium chloride</td>
</tr>
<tr>
<td>DoTAOH</td>
<td>Dodecyltrimethylammonium hydroxide</td>
</tr>
<tr>
<td>DoTAPA</td>
<td>Dodecyltrimethylammonium polyacrylate</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal close-packed</td>
</tr>
<tr>
<td>LCAO</td>
<td>Linear Combination of Atomic Orbitals</td>
</tr>
<tr>
<td>RIXS</td>
<td>Resonant Inelastic X-ray Spectroscopy</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small Angle X-ray Scattering</td>
</tr>
<tr>
<td>SXA</td>
<td>Soft X-ray Absorption</td>
</tr>
<tr>
<td>SXE</td>
<td>Soft X-ray Emission</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
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</table>
Introduction

The material constituents of ourselves could to the predominant part be classified as water, aqueous mixtures and/or moist soft matter systems. Furthermore the most of our surrounding could be categorized in the same way exemplified by the biological systems, seas, lakes and water courses, clays and soils, the atmosphere and not the least foods and drinks, including medications. Also in various industrial processes, water, aqueous mixtures and moist systems are essential parts. The results of studies and understanding of moist systems and aqueous mixtures have thus their use in chemical, biological, meteorological and soil sciences with further applications in environmental sciences, industrial processes and pharmaceutics.

The modelling and understanding of such systems are in many ways challenging by their complexity, due to irregularities, dynamics and random character. This is in contrast to more regular systems like pure crystalline solids or in gases where the single molecules can be seen as solitaires.

For solid and gaseous systems, therefore, more often mechanistic models can be developed leading to closed mathematical expressions or expressions requiring numerical methods, while for liquid systems one is more often obliged to resort to simulation models or statistical/semiempirical models. For the latter types of models it is in general harder to get a perspicuous interpretation and/or they are computationally more demanding than the former types of models.

There are a variety of experimental methods appropriate for material studies that give a picture of the system on the molecular level, such as spectroscopy using electromagnetic radiation in various energy ranges, mass spectroscopy and diffraction methods. Other methods, such as dielectric spectroscopy and thermodynamic measurements, primarily give macroscopic properties such as enthalpy, flow and conductivity, and, by model assumptions, suggest descriptions on the molecular level, for instance in terms of binding energies and mobility of ions.

Compared especially to the study of solid samples, studies of water containing systems are experimentally demanding due to the handling of samples, e.g. by problems with keeping a liquid from running off, maintaining the humidity in a sample or, in cases of liquids with relatively high vapour pressure, to prevent the sample from evaporating, or problems of keeping the low pressure required in many experiments.
Figure 1. Schematic 2D representation of a substance in (A) crystalline, (B) liquid and (C) gaseous phase. The molecules are symbolized by grey spheres and the region of influence, e.g. the distance within which the surrounding gives significant influence on the central molecule, is marked by red circles. As seen, the surrounding within which the region of influence is identical in the crystalline as well as in the gaseous system at the four indicated sites, whereas they are different in the liquid system. Thus, in some aspects, the interaction with the surrounding affecting one molecule could be regarded as identical on every molecule in the crystalline and gaseous system respectively, while in the liquid system an ensemble of several molecules, with different interaction with the surrounding, would be needed to model that system with the same accuracy.

This thesis concerns surfactant micelle systems: a subdivision of the huge class of moist and aqueous soft matter systems. By soft X-ray spectroscopy, dielectric spectroscopy and modelling the molecular arrangement, electronic structure and transport properties of surfactant micelle systems and the constituents thereof have been studied.

I find the engagement in the field of moist and aqueous soft matter systems important as well as scientifically and technically challenging, and I believe that this work can bring some contributions to this research field.
2. Background

This chapter deals with water as well as amphiphilic molecules and carboxylic acids and their interaction with water. It contains a survey of established knowledge, established and debated models, questions and applications of these types of compounds and mixtures.

2.1 Water

The water molecule consists of an oxygen atom covalently bonded to two hydrogen atoms. The molecule is not linear and the electron distribution is strongly displaced towards the oxygen atom which gives the molecule a strong dipole moment ($\mu_{dip} \approx 1.9$ D) and it is even stronger for water in liquid phase. The arrangement also makes the molecule forms hydrogen bonds with high bonding energies ($H_b \approx 20$ kJ/mole $\approx 200$ meV/bond) [Suresh and Naik (2000)] and a possibility to bind in four directions.

![Water molecule structure formula](image)

*Figure 2.* The water molecule structure formula (A). The H – O – H angle ($\theta$) is slightly different in ice, bulk liquid water and gas and varies in the regime 109.5° (ice) to around 104.5° (gas and liquid). The strong polarization makes the water molecule prone to form hydrogen bonds in four directions (B) where two hydrogen bond possibilities are directed along the two oxygen hydrogen axes (hydrogen donor) and two in the symmetry plane cutting the molecule between the hydrogens and linked to the orbital of the lone electron pair (hydrogen acceptors), here denoted by yellow arrows. The water molecules may therefore coordinate up to four other water molecules (C).

In crystalline water (ice), under atmospheric pressure and moderate temperatures, each molecule coordinates to four other water molecules by hydrogen bonds in four directions in a tetrahedral arrangement. In liquid water, how-
ever, the picture is not that clear. Regarding the character of bonding, dynamics, structure, coordination and near ordering, different models have been presented and the matter is at present still lively debated [Luck (1998), Keutsch and Saykally (2001), Kotzmutza et al. (2003), Kashtanov et al. (2004), Wernet et al. (2004), Smith et al. (2006), Fuchs et al. (2008), Tokushima et al. (2008), Odelius (2009), Stokely et al. (2010), Nilsson and Pettersson (2011)].

By its properties, water also shows up an interesting phenomenology in its interaction with other molecules in solutions and moist systems. Studying such systems, besides the gain of knowledge of the systems in themselves, complementary knowledge of the water molecule itself could be obtained. For instance, for water molecules confined in highly packed systems, such as high concentration micelle systems (see below) or clays, the confinement is expected to strongly change dynamics, structure, near order and coordination.

2.2 Micelle gel systems

Surfactants may be described as amphiphilic molecules, i.e. molecules with a hydrophilic and a hydrophobic part (fig. 3). The classification of hydrophilicity and hydrophobicity of the different molecular parts is due to high or low interaction energies respectively, towards the water molecule. For many surfactants in aqueous mixtures, the amphiphilic properties make it energetically favorable for them to cluster into micelles, turning the hydrophobic parts towards each other and turning the hydrophilic part towards water molecules (fig. 4). This phenomenon appears when the surfactant concentration exceeds the critical micelle concentration (CMC). Then the energetic gain of clustering balances the entropic gain of homogeneous distribution in the solution [Israelachvili (2011)]. Micelles might take various geometrical shapes such as spheres, cylinders, sheets, hollow spheres (vesicles), liposomes or branched twig-like cylinders. The micelle shape is a matter of concentration of surfactant as well as the geometrical shape of the surfactant molecule in itself, and also of the degree of repulsion of the charged or strongly polar hydrophilic part [Tanford (1974), Israelachvilli et al. (1976), Holmberg et al. (2003)]. At very high concentrations, i.e. when micelles come in close contact, they may arrange into crystal-like lattices (liquid crystals) (fig. 5) [Holmberg et al. (2003)].

Amphiphilic drugs such as chlorpromazine, promethazine and adiphenine can be classified as surfactants and can also form micelles [Attwood et al. (1996)]. Furthermore, in common with small globular proteins, surfactant micelles of ionic species can be seen as macroions. In these aspects surfactant micelles can therefore be useful as models for the structurally more complicated small globular proteins. An important application for drug for-
mulations are mixed surfactant systems, i.e. formulations where the surfactant drug is mixed with a co-surfactant resulting in mixed micelles [Paulsson and Edsman (2001), Bramer et al. (2003), Bramer et al. (2006)]. By varying the proportions of the constituting surfactants, the equilibrium condition between monomer fraction and molecules in micelles, and thereby the release rate of the drug can be controlled.

Another potentially important application of surfactants is found in drug formulations which involve proteins. Denaturation of proteins, e.g. by enzymes or by the acid environment in the stomach, is a common problem. However, it has been demonstrated that proteins are protected from denaturation by forming complexes with oppositely charged poly-ions and maintain their activity in and after being released from such complexes. Complexes between charged polymers and oppositely charged macroions have also drawn attention as potential vehicles for targeted drug delivery, facilitating the administration of labile or highly toxic drugs [Eichenbaum et al. (1999), Kiser et al. (2000), Kabanov et al. (2004), Nayak et al. (2004), Zhang et al. (2006)].

Mixing a micelle system with poly-ions of opposite charge sometimes result in a more stabilized system giving a two phase water – water/micelle/poly-ion system [Thalberg and Lindman (1993), Skepö and Linse (2003), Hans-
son (2009)] allowing higher water content in the water/micelle/poly-ion phase (fig. 5). Depending on various factors such as pH, temperature and small-ion content, such complexes can reach different degrees of compactness/swollenness, determining the surfactant binding in the complex [Thalberg and Lindman (1993), Biesheuvel and Cohen Stuart (2004)]. To control the surfactant release rate from such a gel complex, it is therefore essential to understand the mechanisms which rule the degree of compactness/swollenness.

**Figure 5.** (A) Illustration of spherical micelle of DoTA-ions wrapped by polyacrylate ion chains (left) and the orthorombic crystalline lattice of such spherical and wrapped micelles. (B) Illustration of cylindrical micelle of DoTA-ions wrapped by polyacrylate ion chains and the hexagonal crystalline lattice of such cylindrical and wrapped micelles (right).

Mechanistic thermodynamic models, such as Poisson - Boltzmann models, Derjaguin-Landau-Verwey-Overbeek (DLVO) models and Monte Carlo simulation models have been used to explain properties like swelling and stabilization of different micelle systems. In the relatively simple Poisson - Boltzmann and DVLO models, the aqueous phase is regarded as a continuum. In these models the influence from water is considered by its permittivity and the charged constituents, by a mean field approach [Biesheuvel and Cohen Stuart (2004), Leal et al (2007)].

In many refined models, using e.g. Monte Carlo or molecular dynamics simulations, the simple ions and poly-ions are discretized but water is still considered as a continuum medium represented by its bulk properties. By this discretization of the ions, i.e. leaving the mean field approximations, correlation effects of the ions appear in the results [Jönsson and Wenner-
Attempts to also incorporate the discreteness of the medium (water) in the modelling have also been made [Pedago et al. (2008), Pedago et al. (2011)]. Experimental evidence on how water and other constituents in the aqueous phase arrange together and with the micelle surface should be essential for understanding such systems and to assess the suggested models. Furthermore, the structuring of water in mixtures with other molecules (lipophilic) could give knowledge about the still puzzling hydrophobic effect and hydrophobic interaction [Israelachvili (2011)].

The formation of a poly-ion surfactant complex by placing a spherical polymer gel in a surfactant solution has been another subject for modelling. In such a system, the surfactant molecules diffuse into the polymer matrix so that a poly-ion surfactant complex forms in a shell. By the supply of surfactant molecules, the shell grows toward the centre of the polymer sphere [Göransson and Hansson (2003) Nilsson and Hansson (2005), Nilsson and Hansson (2008)].

Equilibrium models of such systems contain elements of fluid mechanics and field theory and the elasticity of the complex are in the models essential [Sekimoto and Kawasaki (1989), Hong et al. (2008), Gernandt (2013)]. The force action, configuration and distribution of configurations on the molecular level can therefore give important contribution to the modelling and understanding of the parameters of the model. When modelling the formation process of such a system [Göransson and Hansson (2003)], also the diffusive properties of the surfactant molecules are essential.

2.3 Carboxyl groups

Carboxyl groups (–COOH) are essential functional parts of a number of compounds of biochemical importance, e.g. polypeptides, proteins, fatty acids, and charged polysaccharides, where they contribute to the high solubility of these molecules in an aqueous environment. The carboxyl group plays vital roles in several biochemical pathways such as the oxidation of fuel molecules in the citric acid cycle, involving several di- and tricarboxylic acid compounds, and also in industrial reactions such as nylon synthesis.

Typically, the acidity of carboxylic acids are high compared with other molecules containing OH bonds, e.g. alcohols, because the electron structure of the COO⁻ group is stabilized by resonance [Mc Murray (2008)]. It is well known that the chemical reactivity as well as related properties, such as the affinity for metal ions (coordination complex formation) and protons (acid-base activity), depend on the local chemical environment of the carboxyl group [Panina et al. (2002), Lee and Crippen (2009)].

A typical monocarboxylic compound like acetic acid has a pKₐ⁻ value of 4.7, while the pKₐ⁻ value of trichloroacetic acid is 0.7. The two pKₐ⁻ values of the dicarboxylic oxalic acid are 1.3 and 4.3, and the polycarboxylic poly-
acrylic acid has an apparent pK\textsubscript{a}-value of about 7 in water [Gregor \textit{et al.} (1955), Gunnarsson \textit{et al.} (1980)]. The large variations in pK\textsubscript{a}-values are mainly due to the bonding energy between the hydrogen and oxygen and entropic effects such as the flexibility of chain structures of the molecules and surrounding water.

Seemingly, in oxalic acid and polyacrylic acid the neighboring -COOH groups cause changes of pK\textsubscript{a} in different directions compared to the pK\textsubscript{a} of the more “neutral” analogues, formic acid and acetic acid (pK\textsubscript{a} ~4.7). Suggested explanations of these effects considers electrostatic effects from charges and electron affinity of the COOH groups [Cumming.\textit{and} Kebarle (1978), Lee \textit{and} Crippen (2009)]. However, a deeper understanding of what determines pK\textsubscript{a} is desirable in the understanding of the behavior and pH dependence of, for instance, proteins and other biomolecules.

\textit{Figure 6.} Structure formulas of the carboxylic group, and some molecules in which this group is a constituent: oxalic acid, polyacrylic acid, glycine, acetic acid and trichloro acetic acid.
This thesis covers studies of water, surfactant gel systems and carboxylic acid solutions by soft X-ray spectroscopy and dielectric spectroscopy. It also includes mechanistic modeling of the release of the non-aqueous components a mixed binary surfactant micelle gel systems.

The aim of the thesis is to investigate properties and mechanisms important for surfactant gel system formation and stability, as well as for surfactant release from a surfactant gel matrix. Furthermore it aims to gain more knowledge about the pKₐ determining factors in organic acids and about the intermolecular bonding in bulk water and water when it is confined.

Soft X-ray spectroscopy requires ultra-high vacuum (UHV) conditions for beamline, synchrotron and instrumentation. This poses a challenge for such measurements on moist and liquid systems, since the sample properties, e.g., the high vapor pressure, seem to be incompatible with UHV. Furthermore, reliable control of sample humidity of the moist samples, as well as reliable continuous sample replacement for the liquids samples, are required for maintaining a high experimental quality. A general aim in the soft X-ray spectroscopy studies of moist and liquid systems is therefore the development of the experimental design, the sample handling and the equipment attached to the end station.
4 Principles and theory of measurements, analysis and experimental set-up

The first part of this chapter deals with the theory of soft X-ray spectroscopy and interpretation of soft X-ray spectra. It is followed by the experimental set-up and the theory of the elements in the experimental set-up. The chapter continues with the presentation of the theory and experimental set-up for dielectric spectroscopy as well as X-ray crystallography. In the last part of the chapter, the theoretical considerations for modelling the release from a two-component composite gel are dealt with, and the set-up for the experiments evaluating the models is presented.

4.1 Atoms, molecules, orbitals and spectra

4.1.1 Theory of orbitals and electronic states

4.1.1.1 The picture of atoms and molecules - electron orbitals and excited states

According to the prevalent picture matter consists of positively charged atom nuclei surrounded by negatively charged electrons. Applying quantum mechanics to that picture and slightly simplifying, the surrounding electrons occupy different orbitals, where each orbital is linked to a certain energy and spatial statistical distribution for the one or two electrons that, by the Pauli principle [Eisberg and Resnick (1974)] can occupy the orbital. For a certain atom or molecule, different configurations of orbitals, so-called states, are possible, where the energy of a state is the sum of the energy of the electrons. The state with the lowest energy is called the ground state, while the other states (of higher energy) are termed excited states.

For one-electron systems such as the hydrogen atom, the electron orbitals and energies are given by solutions of the time-independent Schrödinger equation [Eisberg and Resnick (1974)]:

\[
\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) + V(x, y, z) \cdot \psi(x, y, z) = E \cdot \psi(x, y, z) \quad \text{eq. 1}
\]

where \( \psi \) is the electron wavefunction, \( m \) is the electron mass, \( V(x,y,z) \) is the potential and \( E \) is the electron energy. When more electrons are included, as
in other atoms and molecules, the picture and the calculations complicate significantly. For many electron systems a more correct treatment uses electronic states and state wavefunctions rather than single electron orbitals. The state wavefunctions are in similarity to the one-electron wavefunction, solutions to equations analogue to eq. 1, but due to the complexity, one is, however, obliged to resort to different approximate and numerical methods.

\[
\begin{align*}
&3p_x \quad 3p_y \quad 3p_z \\
&3s \\
&2p_x \quad 2p_y \quad 2p_z \\
&2s \\
&1s
\end{align*}
\]

*Figure 7.* Illustration of the spatial distribution of different electron orbitals and corresponding energy level diagram of orbitals.

### 4.1.1.2 The Linear Combination of Atomic Orbitals method (LCAO-method) view as a model for qualitative reasoning

An early developed method for calculating molecular orbitals is the Linear Combination of Atomic Orbitals method (LCAO method) [Karplus and Porter (1970)]. Despite its simplicity, compared to later developed and more sophisticated methods, it can nevertheless serve for comprehensible qualitative reasoning about orbitals, bonds, excited states and transitions between different states. In the LCAO method, approximate solutions (i.e. molecular orbitals) of the Schrödinger equation are obtained by linear combinations of a basis set of atomic orbitals of the interacting atoms.

Depending on the number of atoms and atomic orbitals contributing, the obtained molecular orbitals can be classified in the following way; i) orbitals mainly consisting of a pure atomic orbitals, localized at the atom in question, ii) orbitals mainly consisting of atomic orbitals from two atoms in a bond and finally iii) delocalized orbitals, where orbitals from all or most of the atoms in the molecule contribute to the molecular orbital. In the two latter categories, the orbitals can further be classified as bonding, anti-bonding or non-bonding, depending on whether the orbital energy is smaller or larger
than the summed orbital energy of the parent atomic. In condensed phases, atomic orbitals from neighbouring molecules may also bring noticeable contributions to the orbital picture. Thus, it is reasonable to assume that different surroundings of a molecule or a certain atom of that molecule will result in slightly different solutions of the Schrödinger equation, i.e. slightly different wave functions and energy levels of the orbitals.

![Figure 8](image-url)

*Figure 8.* Illustration, by energy level diagrams, of the idea of LCAO formation of molecular orbitals from atom A and atom B. Atomic orbitals, whose energy levels are marked with grey bars, form, by linear combination, molecular orbitals whose energy levels are marked with black bars. As a rule of thumb, atomic orbitals of similar energy in the two atoms are prone to combine (here illustrated by thin solid lines) to molecular orbitals, but in general also other orbitals of the bonding atoms contributes (here illustrated by dashed lines).

As mentioned above, the LCAO method is a relatively simple method. One of its main shortcomings, is that it uses a mean field approximation of the electrons when calculating the potential function [Engel (2010)]. In state-of-the-art methods, direct electron - electron interaction (electron correlation) or other compensations for the mean field approximation are made. Examples of such methods are Configuration Interaction, Møller-Plesset, and Density Functional Theory methods [Engel (2010)].

4.1.2 Soft X-ray spectroscopy

The interaction between electromagnetic radiation and matter, manifested in the ability of materials to absorb and scatter the radiation, can be understood
by considering the electromagnetic nature of the radiation and the view that matter consists of electrically charged particles. Incoming electromagnetic radiation may, if the radiation is of appropriate energy, induce a change of the electronic state of an atom or molecule. In a simplified picture this can be regarded as a change in occupation of the orbitals (fig. 9A).

In soft X-ray spectroscopy, electromagnetic-radiation induced transitions of electrons between different orbitals are studied. By appropriate choice of energy of the exciting electromagnetic radiation, the excitation of an electron from a core orbital to an unoccupied orbital is induced. The obtained core hole can be filled by a valence electron in a subsequent deexcitation process. In X-ray Absorption Spectroscopy (XAS) experiments, the sample is exposed to X-ray radiation scanned in the desired energy range and absorption peaks are obtained at energies corresponding to the differences between the ground state and different excited states. In Resonant Inelastic X-ray Spectroscopy (RIXS) experiments, the sample is exposed to X-ray radiation with one or a series of distinct energies, e.g. at the absorption resonances (peaks), and spectra of the radiation emitted in the deexcitation process are recorded.

In the excitation process, X-ray radiation is absorbed at energies reflecting the differences between the unoccupied orbital energy and core orbital energy (fig 9). Applying a quantum mechanical representation of electromagnetic radiation [Sakurai (1973)], the absorption transition cross section \(I_{abs}\) can be described by Fermi’s golden rule:

\[
I_{abs} \propto \left| \langle \Psi_f | T_{op} | \Psi_i \rangle \right|^2 \delta(E_f - E_i - \hbar \omega)
\]

where the notation \(\langle \Psi_f | T_{op} | \Psi_i \rangle = \int \Psi_f(T_{op} \cdot \Psi_i) dv\), and is termed the matrix element, \(\Psi_f\) is the final state wave function, \(E_f\) is the final state energy, \(\Psi_i\) is the initial state wave function, \(E_i\) is the initial state energy, \(\hbar \omega\) is the energy of the exciting radiation and \(T_{op} = e \cdot \vec{r}\) is the dipole operator.

In the deexcitation process, X-ray radiation is emitted at energies reflecting the differences between the valence orbital energy and core orbital energy (fig 9). It is tempting to see excitation and deexcitation in this way, as two separated processes occurring each with probabilities according to Fermi’s golden rule (fig. 9A). This is sometimes also a good approximation. However, the excitation and deexcitation is more correctly described as a one-step process, i.e. the absorption and emission occur in the same process and it is sometimes required that this more sophisticated description is used (fig. 9B). Here, it should also be noted that such a process may include additional excitations and deexcitations, e.g. vibronic, as well as many-step processes by cascades of intermediate states.
Electron transition probability \( I \) can, in the one-step view, after some approximate considerations be described by the Kramers-Heisenberg equation:

\[
I \propto \left| \sum_j \frac{\langle \Psi_f | T'_{op} | \Psi_{cj} \rangle \langle \Psi_{cj} | T_{op} | \Psi_i \rangle}{\hbar \omega - (E_{cj} - E_i) + i\Gamma/2} \right|^2 \delta(E_f - E_i - \hbar \omega + \hbar \omega') \quad \text{eq. 3}
\]

where \( \Psi_{cj} \) is the intermediate state wave function, \( E_{cj} \) is the intermediate state energy, \( \hbar \omega \) is the energy of the exciting radiation, \( \hbar \omega' \) is the energy of the emitted radiation, \( T_{op} \) is the dipole operator of the exciting radiation, \( T'_{op} \) is the dipole operator of the emitted radiation and \( \Gamma/2 \) is the energy broadening of the absorption peak due to core hole lifetime (i.e. the core hole lifetime equals \( \hbar / \Gamma \)). The derivation of eq. 3 is resting on the time-dependent Schrödinger equation, a quantum mechanical formulation of electromagnetic radiation and perturbation theory [Sakurai (1973)].

**Figure 9.** Illustration, by energy level diagrams, of the excitation-deexcitation processes. A) In case of two-step process with i) the initial state, ii) the intermediate state with a core hole and an electron in the formerly unoccupied orbital and iii) the final state, where the core hole has been filled by a valence electron leaving an electron hole in a valence orbital. B) In case of the one step process with i) the initial state, and ii) the final state with an electron in the formerly unoccupied orbital and an electron hole in a valence orbital. Excitation by and emission of electromagnetic radiation (photons) are symbolized by wave arrows.

What can be read out of eq. 3 is that the emitted energy is linearly dependent of the exciting energy rather than being the energy difference between the intermediate state and final state as in the two-step picture (eq. 2). Furthermore, the summation over \( j \) in eq. 2 indicates that the final state might be reached via several intermediate states. In cases where the lifetime energy broadening is similar to the energy separation of different absorption reso-
nances, the intermediate states that these resonances reflect will participate in the transition. Intensity calculations according to the two-step view, by summing over excitation-emission probabilities associated with each specific intermediate state, will then be incorrect and the intensity has to be calculated according to the more adequate eq.3.

Figure 10. Figure illustrating a qualitatively reasoning of angular anisotropy of emission in RIXS. In liquids and gases molecules will orient randomly. Imagine an unoccupied orbital of a certain symmetry. i) Some molecules will orient so that the orbital in question, here symbolized by ovals, having the same direction as the polarization (E-field) of the incoming X-ray radiation. By classical manner (antenna principle), this orbital is likely to participate in an electron transition (if the photon energy is appropriate) and a high absorption crosssection is expected and in turn, a high intensity of the emitted radiation. ii) In case the deexciting valence orbital is of same symmetry, i.e. having the same direction as the polarization (E-field) no radiation will be emitted in the polarization direction but the emission intensity will have a maximum (here indicated by arrows) perpendicular to the polarization. iii) In case the deexciting valence orbital is of different symmetry, i.e. having the direction perpendicular polarization (E-field), radiation will be emitted preferentially in the polarization direction.

Dipole transitions are governed by the symmetries and spatial overlap of the involved orbitals. Sometimes the matrix elements are evaluated to be zero for symmetry reasons. In the dipole approximation, transitions are only possible between atomic orbitals where the angular momentum quantum number, \( l \), differs by +/-1 [Eisberg and Resnick (1974), Powel and Craseman (1961), Sakurai (1973)]. For excitation at the K-edge, the core orbital is almost identical to the atomic 1s orbital. Using the LCAO picture of molecular orbitals, the probability for transitions involving the core orbital is determined by the \( p \) character of the valence or unoccupied orbitals, i.e. the contribution of atomic \( p \) orbital in the linear combination forming the orbital (projection of molecular orbital into \( p \) orbital). Besides, the intensity of emitted radiation is different in different directions relative to the polarization of exciting X-ray radiation by the mutual symmetry of orbitals involved in the

The photon absorption and emission processes may also excite vibrations [Werme et al. (1973), Rubensson et al. (2012). Vibration-specific features will in such cases influence absorption spectra sometimes manifested in vibrational fine structure. At moderate resolution, additional vibrational excitations reveal themselves by additional energy losses and broadening of the spectral features.

An undoubtedly important advantage with XAS and RIXS is the element selectivity [Stöhr (1992)]. More precisely, that is due to high transition probabilities of core excitations of certain elements at certain energy ranges. For carbon such a range is 280 – 310 eV, for nitrogen it is 390 – 415 eV and for oxygen it is 520 – 550 eV. Scanning such a range, the researcher knows that mainly a certain atom species is excited and in the case of other atoms excited at these energies, the excitations are to continuum states (ionization) and will appear as a featureless and easily compensable background. Atom selectivity in the emission spectra is similarly achieved. Since deexcitations from the valence orbitals to the core level are expected to be slightly lower than the excitation energies, deexcitation from just a certain atom species will be recorded by choosing an inappropriate energy range for detection.

4.1.3 Spectral shifts due to different environments

In summary, the electronic structure rules chemical properties of atoms and molecules, i.e. how they interact and bind to other atoms and molecules, and conversely, the surrounding will affect the electronic structure of atoms and molecules. This means that the electron structure and orbital energy levels are intimately linked to the atoms in the near surrounding (fig. 11), either chemically bonded (intramolecular bonds) or just physically near, as in mixtures (intermolecular bonds). On a quantum mechanical level, it is no strict qualitative difference between these interactions but the categorization is often practical.

From XAS and RIXS measurements, molecular and intermolecular structures of the systems studied can be determined, e.g. from ab initio or by an Ansatz method using e.g. Density Functional Theory (DFT). By the Ansatz method, qualified suggestions of atomic and molecular configurations are made for which orbitals and possible excited electronic states can be determined. By Fermi’s golden rule and the Kramers-Heisenberg equation, both the energies and the probabilities of transitions at certain energies of incoming radiation can be calculated. Absorption cross sections and emission intensities can be achieved from these probabilities (related to the intensities of the measured spectra) and compiled into simulated spectra. By comparing to measured spectra, a suggested atomic configuration can be tested.
Figure 11. Illustration of the energy shifts of orbital energy levels caused by different surroundings, in this figure schematically represented by a water molecule in a) water environment (red energy level lines) and b) trimethylammonium charged group and chloride ion environment (black energy level lines).

4.2 The synchrotron, beamline and end station

In soft X-ray spectroscopy it is desirable that the X-ray radiation probing the sample is of high intensity, energetically well resolved, tuneable and well focussed. This puts demands on the radiation source regarding the power \( P \) radiated, the spectral bandwidth, the area \( A \) it radiates from and the solid angle \( \Omega \) it radiates into. In these connections, the spectral brilliance [Attwood (2007)] is a relevant measure that combines these properties and is defined by:

\[
B_{\Delta\omega/\omega} = \frac{\Delta P_{BW}}{A \cdot \Omega}
\]

where \( \Delta P_{BW} \) is the radiated power within a certain relative band width, commonly chosen to be 0.001.

4.2.1 The synchrotron

X-ray radiation can be generated in various ways. Common for all types of generation of electromagnetic radiation is that the source is an accelerating charge. It can, by classical electrodynamics, be shown that the intensity of the emitted radiation is proportional to the square of the acceleration \( a \) and \( \sin^2 \Theta \), where \( \Theta \) is the angle between the propagation direction of the radiation and the direction of acceleration [Panofsky and Phillips (1962)]. For a sinusoidal acceleration of an electron, the emitted power per solid angle \( dP/d\Omega \) is given by the equation [Attwood (2007)]:
\[
\frac{dP}{d\Omega} = \frac{e^2 a^2}{16 \pi \varepsilon_0 c^3} \sin^2 \Theta \quad \text{eq. 5}
\]

The present state of the art soft X-ray spectroscopy research is using synchrotron radiation. Synchrotrons can offer polarized electromagnetic radiation which is easy to tune energetically. Compared to the simpler designed X-ray tubes, used today e.g. in medical applications and for simpler X-ray diffraction measurements, the brilliance of the source and the intensity [Attwood (2007), Ladd and Palmer (2003)] of the generated radiation is orders of magnitude higher. For a synchrotron as source of X-rays, generation rests on acceleration of free electrons moving at speeds near the speed of light in a closed trajectory in the synchrotron storage ring.

If applying a magnetic field across an electron beam, the Lorenz force will cause the electrons to deflect perpendicular to the beam and the direction of the magnetic field (fig. 12). By aid of a so-called bending magnet, this effect is used to get the closed electron trajectory in the storage ring. The electron beam going through the magnetic field of the bending magnet will make a bend and it is thus possible to form a closed polygon-like trajectory with straight sections and bends (fig. 12).

Figure 12. Schematics a of synchrotron storage ring with bending magnet and undulator insert. The bending magnet enlargement is illustrating an electron trajectory in a magnetic field, where the electron is deflected by the Lorentz force.

The Lorentz force effect is also for used for generating electromagnetic radiation by the also implied acceleration of the electrons. An insertion device providing magnetic fields designed to generate radiation with desired properties can be placed in a straight section of the synchrotron ring. Since there are several straight sections in the synchrotron, radiation generating insertion
devices can be inserted at several places in a storage ring. The radiation from each such insertion device is directed into a beamline and further to an end station where the sample under study is placed.

A beamline is in general intended for certain types of experiment, and designed to obtain radiation fulfilling specific experimental requirements. Those requirements rule the design of the synchrotron insert as well as optical elements like gratings, mirrors and slits in the beamline. For the purposes of soft X-ray spectroscopy, the important parameters are energy range, energy resolution, intensity, polarization and focus.

4.2.2 The undulator

At beamline 511[Denecke et al. (1999)] at MAX-lab, Lund [http://www.maxlab.lu.se], where the synchrotron based experiments were performed, the insertion device for X-ray generation is a so-called undulator. This undulator is designed with a number of bending magnets arranged in a plane array and oriented so that neighbouring bending magnets have oppositely directed magnetic fields (fig. 12). The undulator is placed in a straight section of the storage ring with the magnetic field perpendicular to the electron trajectory. When passing the undulator, the electrons will undulate, due to the Lorentz force, in a nearly sinusoidal trajectory and by the corresponding nearly sinusoidal acceleration pattern, the electrons will emit a narrow frequency band of plane-polarized electromagnetic radiation.

The axial velocity ($v_a$) of the electrons, i.e. the velocity along the undulator, is highly relativistic and typically >0.9999995c, leading to the, in relativistic connections, useful Lorentz factor ($\gamma$) taking values >1000. The relativistic effects that this will cause are of vital importance for the high brilliance of the source. The emitted power is increased by a factor $\gamma^2$ by time dilation compared to a classic situation with oscillating electrons having non-relativistic axial speed, [Attwood (2007)]. Furthermore, due to Lorentz contraction, the radiation pattern, i.e. the directional dependence of emitted intensity, is deformed in a favourable way. What is radiated in the half-space in forward direction of the electron under classical conditions, is under relativistic conditions radiated within a cone of solid angle $\pi/\gamma^2$. The total relativistic effect on the brilliance is thus an increase of a factor of $\sim \gamma^4$.

The wavelength of the emitted radiation is also strongly affected by relativistic effects as well as Doppler shifts and is given by the undulator equation:

$$\lambda = \frac{\lambda_u}{2\gamma^2} \left(1 + \frac{K^2}{2} + \gamma^2 \theta^2\right)$$

where $\lambda_u$ is the double of the spacing (undulator periodicity) between two neighbouring magnets in the undulator, $\theta$ is the radiation angle relative $v_a$, eq. 6

$$\theta = \frac{\lambda}{v_a}$$
\[ K = eB_0 \lambda / 2m_c c, \quad B_0 \] is the magnetic field amplitude and \( m_c \) is the electron mass.

The wavelength, and thereby the frequency (energy), is easily tuned by changing the magnetic field of the undulator. If, for instance, the magnetic field of the undulator is increased, the transverse movement and velocity \( (v_t) \) of the electrons will increase and the axial velocity \( (v_a) \) of the electrons will consequently decrease. By this, \( \gamma \) will decrease, implying an increased wavelength according to eq. 6.

4.2.3 Beamline optics

The beam leaving the undulator has a certain bandwidth. One of the main reasons for this is the dependence between the radiation angle \( \theta \) and the wavelength of the emitted radiation by Doppler shift, expressed by the undulator equation above. The bandwidth is also limited due to the finite undulator length and is expressed as \( \Delta \lambda / \lambda = 1/N \), where \( N \) is number of periods in the undulator.

For XAS and RIXS experiments, further monochromatization of the emitted radiation is in general required. At beamline 511 [Denecke et al. (1999)] at MAX-lab [http://www.maxlab.lu.se] this is accomplished by a plane grating monochromator using the relation between wavelength \( \lambda \) and the incidence \( (\theta_i) \) and exit \( (\theta_e) \) angles of the beams measured relative to the surface normal for constructive interference [Peatman (1997), Hecht and Zajac (1980)]:

\[ m\lambda = s \cdot (\sin \theta_i - \sin \theta_e) \quad \text{eq. 7} \]

where \( m \) is an integer (order of reflection), and \( s \) is the groove spacing.

An exit slit is placed some distance away from the grating. By an arrangement of mirrors and the grating, radiation of different wavelengths are focussed on different points on the exit slit plane according to \( \theta_i, \theta_e \) and eq 7. Radiation of a specific wavelength will focus on the slit and pass through to the sample while radiation of lower and higher energies focus beside the slit and are stopped. To achieve that radiation of desired wavelength (and energy) hits the slit and to further be guided to the sample, the grating is turned so that the parameters \( \theta_i \) and \( \theta_e \) fulfil eq.7. By another set of mirrors (Kirkparick-Baez mirrors), the beam exiting the slit is re-focused on the sample (fig. 13).

By the finite slit width, the edges of the slit will correspond to slightly different exit angles of the grating and with that, slightly different wavelengths. The relation between exit angle difference \( (\Delta \theta_e) \) and bandwidth \( (\Delta \lambda) \) can be calculated by differentiating eq. 7 above with respect to \( \theta \) and rearrangement gives: \( |\Delta \lambda| = \Delta \theta_e \cdot s \cdot (\cos \theta_e) / m \). The bandwidth of the beam pass-
ing the slit is therefore dependent on the slit width, where a narrower slit will give a narrower bandwidth by the cost of less photon flux of the beam.

*Figure 13.* Schematic figure of the beamline monochromator with a grating, focussing mirrors and a slit. The beam from the undulator is entering from the left in the figure. Radiation of different energy, here represented by green red and blue rays, is focussed on different positions on the slit plane. By appropriate choices of $\theta_{in}$ and $\theta_{ex}$, radiation of desired energy (green) will focus on the slit and pass through to the sample while radiation of lower and higher energies (red and blue) will focus beside the slit and be stopped.

4.2.4. The end station

4.2.4.1 Low pressure requirements

Ultra high vacuum conditions in the synchrotron ring ($\sim 10^{-9}$ mbar) as well as in the beamline and end station ($\sim 10^{-8} - 10^{-9}$ mbar) are required to obtain a reasonable lifetime of the electron beam in the synchrotron ring and to avoid oxides and other contaminants on the radiation reflecting elements in the beamline. Furthermore some of the detectors also require a low pressure to not be damaged when measuring. The ultra high vacuum is achieved using different types of pumps, e.g. turbo pumps, displacement pumps and ion pumps.

4.2.4.2 The sample cells

For easily evaporated samples such as gels or solutions it is necessary to isolate them from the vacuum in the experiment chamber. One way of doing this is to put the sample in a sample cell equipped with an ultrathin X-ray transparent carbon or silicon nitride window. The window allows the sample to be available for X-ray exposure [Forsberg (2009)]. Narrow tubes leading from the exterior of the experimental chamber are attached to the cell. The whole arrangement is mounted to a manipulator, allowing the sample cell to be moved horizontally and vertically and turned around the vertical axis.
Figure 14. Cutaway and exploded view drawings of the liquid sample cell (A) and the solid sample cell (B). Each sample cavity (encircled with green) is delimited to the vacuum in the experiment chamber by a thin carbon window on a silicon substrate (blue). The sample cavity is vacuum-gasketed with aid the front plate and viton rubber gaskets (black). In the solid sample cell (B), the sample is placed in the sample holder (yellow). The liquid (A) and humid gas (B) flow through each sample cavity are supported via the pipes (brown) that are attached on the top of the cell and further connected to the sample cavity by drilled channels in the sample cell material.

For liquid samples, a liquid flow is applied through the tubes, continuously changing the sample in the cell (fig 14 A). This has several advantages; it is easy to change the samples, it compensates for possible losses of sample evaporating away through minor leaks, in case of radiation damage, it provides a continuous change to fresh sample, and if decay products adheres to the window these can be washed away by the flowing liquid. The flow is maintained by a peristaltic pump (fig.15 A).

For humid solid samples, e.g. gels, a sample cell equipped with a sample holder is used (fig. 14 B). The sample holder has a shallow (~0.2mm deep) indentation, where the sample is placed, and is threaded into the sample cell material, providing the opportunity to adjust the sample surface close to the cell window. A humidified gas flow (He or N₂) can be applied through the tubes between the exterior of the experimental chamber and the sample cell. The humidity of the sample can be controlled by choice of relative humidity of the gas by the equilibrium condition between the relative humidity of the gas and the sample humidity. The thermodynamic equilibria between water content in the sample substance and the surrounding atmosphere at different relative humidity have been determined in a separate experiment by VTI 100 Sorption analyzer.
To protect sensitive components in the experimental chamber from accidental high pressure, e.g. in case of window rupture, the tubes are equipped with interlocked solenoid valves triggered via a sensor, if a critical pressure is exceeded in the experimental chamber.

Figure 15. Schematic figure of the gas humidity system (A) and liquid flow system (B).

4.2.4.3 The humidity system
A gas flow driven by the over pressure from a gas tube and regulated by a regulator is divided into two branches; one dry and one that is saturated with humidity by letting the gas through liquid water (fig. 15 B). These sub-flows are then mixed in a switch valve and the resulting humidity is set by a duty cycle between humidified and dry gas. This mix is then guided through the sample cell, keeping the sample in an atmosphere of controlled relative humidity. The relative humidity of the flowed gas is measured by sensors placed just before the entrance and just after the exit of the sample cell system. There is a difference between the relative humidity at the entrance and the exit due the pressure fall in the system. In a control experiment where a humid sensor also was placed in an empty sample cell, it has been concluded that the relative humidity in the cell equals the average of the relative humidity of the gas at the entrance and at the exit. The gas flow system is also equipped with a pressure sensor in order to monitor the over pressure. Sensor recording, monitoring and control of the dry gas/humid gas switch are done
by a LabVIEW based program and an AD/DA-board. The humidity is set by manually regulating the duty cycle until the desired cell humidity is reached.

### 4.2.4.4 The XAS measurements

The most straightforward way to measure XAS would be to place the sample between the incoming beam and the detector, and record the intensity of the beam that passes through the sample and relate it to the intensity of the incoming radiation. However, this would require very thin samples with dimensions in order of magnitude of the attenuation length of 100 nm. To avoid this requirement, absorption is measured indirectly by the intensity of the fluorescence yield, i.e. the secondary emitted photons following the absorption.

The principle for absorption measurement in this way is that incoming radiation with energies where the absorbance is low will, to a higher extent, penetrate deeper into the sample than incoming photons with energies where the absorbance is high. The deeper the absorption occurs, the longer path the secondary emitted radiation has to travel in the sample material before reaching the detector and thereby it will be more absorbed and a smaller intensity will be registered. Thus, the smaller the absorbance is, the lower intensity of the secondary radiation will be recorded (fig. 16).

![Figure 16](image)

*Figure 16. The principles for measuring absorption by fluorescence yield: The deeper the incoming beam penetrates the sample (low absorption), the less emitted radiation reaches the detector due to longer exit path and exponential decrement of intensity.*

Some phenomena have to be regarded in XAS measurements by fluorescence yield. The measured intensity is not in general proportional to the absorption of the incoming radiation, which means that the relative intensity of the peaks in a fluorescence yield spectrum can not directly be related to the relative absorbance of the incoming radiation. The relative fluorescence intensity is also dependent of incidence and exit angles in the sample of the
incoming and the secondary emitted radiation respectively, and at very flat incidence angles the intensity does hardly vary at all with different absorption (saturation) [Eisebitt et al. (1993)].

4.2.4.5 The RIXS measurements

The principal parts of the grazing incidence spectrometer are an entrance slit, a grating and a MCP detector. These are geometrically arranged so that the Rowland condition is fulfilled [Rowland (1902)], i.e. they are placed tangentially on a circle of specified radius ($R_{\text{Row}}$) and the spherical grating has the radius $2R_{\text{Row}}$ (fig. 17). This geometrical arrangement ensures that radiation of certain energy is focussed on the detector, in general forming slightly curved lines, on the detector surface. Spectra are recorded by, for each energy, summing photon counts from such focal lines. The slit and grating are also arranged to give a grazing incidence angle of the grating to obtain high reflectance in the soft X-rays region. The spectrometer used at beamline 511-3 (MAX-Lab) (Grace IV, Scienta) [Nordgren et al. (1989)] is equipped with three gratings optimized for measurements in different energy ranges. The gratings are selected by baffle settings shadowing the gratings not used.

![Figure 17. Schematic figure of grazing incidence spectrometer using the Rowland condition. The entrance slit, grating and detector are placed on a circle (black dashed line) of specified radius (R) The grating in turn is bent as a section of a sphere (grey dashed line) with radius 2R.](fig17.png)

The slit-limited resolution ($\Delta E$) of the spectrometer is ruled by the energy of the radiation ($E$), the slit width ($w$), the separation of grooves ($s$), the radius of the grating and the diffraction order ($m$). This relation is with good approximation expressed as: [Nordgren and Guo (2000)]

$$\Delta E(eV) = \frac{E^2(eV)}{12400} 10 \frac{w(\mu m)s(mm)}{mR_{\text{Row}}(m)}$$  \hspace{1cm} \text{eq. 8}
where the units that are to be used for the different quantities are given in the parentheses. However, the maximum attainable resolution is limited by the spatial resolution ($\Delta z_{\text{res}}$) of micro channels on the detector. The smallest reasonable slit width, i.e. where slit width energy resolution reaches detector energy resolution is given by

$$w \approx \frac{\Delta z_{\text{res}} \cdot \cos \theta_{\text{ex}}}{1.1}$$

where ($\theta_{\text{ex}}$) is the exit angle of the beam measured relative to the surface normal of the grating. The total resolution of a RIXS spectrum is also dependent of the bandwidth of exciting radiation. In case of one-step exciting-deexciting process, with short lifetime of the intermediate states, the emitted energy disperses with the exciting energy according to the Kramers-Heisenberg equation (eq. 3). In that case the bandwidth of the emitted radiation will be the same as the bandwidth of the exciting radiation and the resulting resolution in RIXS spectra is determined by convolution of the incoming bandwidth and spectrometer bandwidth.

### 4.2.5 Description of the soft X-ray experiments

A multichannel plate (MCP) detector was placed in the end station chamber making 45° angle relative to the incoming beam seen from the sample. This detector was used for XAS measurements by fluorescence yield in the experiments. A spectrometer, used for RIXS measurements, was mounted perpendicular to the incoming beam seen from the sample. With aid of the manipulator, the sample could also be turned, making appropriate incidence and exit angles for XAS and RIXS measurements respectively (fig. 18).

*Figure 18.* Schematics of the end station geometry at beamline 511-3 at MAX-lab. The incoming beam hit the sample, which absorbed and reemitted radiation. The MCP detector and spectrometer were mounted at fixed angles (45° and 90° respectively) relative the incoming beam. By turning the sample counterclockwise (typical position symbolized by the grey box) the secondary radiation could be recorded by the MCP detector (XAS-measurements). By turning the sample clockwise (typical position symbolized by the diagonal striped box) the secondary radiation could be recorded by the spectrometer (RIXS-measurements).
4.3 Dielectric spectroscopy

Dielectric spectroscopy can be used to investigate the dynamics of bound and mobile charges in solid and liquid materials. In low-frequency dielectric spectroscopy (LFDS), sinusoidal ac voltages with frequencies in the MHz – mHz range are applied across the sample under study. In the electric field, charges and dipoles in the sample will move and turn, affecting the response current in the circuit.

![Diagram of dielectric spectroscopy](image)

*Figure 19.* Principles of dielectric spectroscopy measurements (A) and the actual set-up (B) [Welch (2006)]. The sample is mounted between two flat electrodes and sinusoidal voltages are applied across the sample. Ions and dipoles in the sample will move and turn due to the applied field. The phase and size of movement - and thereby the circuit current - are dependent of applied frequency, the interaction with the environment and inertial parameters of particles. The current is also dependent on sizes and numbers of charges and dipoles. The electrodes (black in panel A) are surrounded by guard ring, (grey in panel A) and a guard circuit to provide a homogeneous electric field in the part of the sample that is measured. The guard electrode set-up required that the guard ring is insulated (white on the right electrode in panel A) from one of the measuring electrodes. The electrode separation is set by a micrometer screw.

The measured response ac current, can be characterized by amplitude and phase relative to the applied ac voltage. A complex representation of the response current and interrelated quantities – i.e. representing the quantity by a complex number rather than by its phase and amplitude – is, however, often more convenient to use in the mathematical treatment in the succeeding analysis. At the different angular frequencies ($\omega$) of the applied ac voltages, complex quantities like impedance ($Z^*(\omega)$) and admittance ($Y^*(\omega)$) can be determined as ratios of the complex currents and voltages. Furthermore, the complex relative permittivity ($\varepsilon^*(\omega)$) and conductivity ($\sigma^*(\omega)$) can be calculated as $\varepsilon^* = \varepsilon' + j\varepsilon'' = Y^* / j\omega C_0$ and $\sigma^* = \sigma' + j\sigma'' = j\omega\varepsilon_0\varepsilon^*$ respectively, where $j = \sqrt{-1}$, $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of the permittivity $\sigma'$ and $\sigma''$ are the real and imaginary parts of the conductivity,
ε₀ is the permittivity of free space (8.854⋅10⁻¹⁴ F/cm), and C₀ the free space capacitance of the measurement electrode set-up (fig. 19)

4.3.1 Theory of dielectric spectroscopy

Charged species like electrons and ions and polar entities will, as stated above, move due to the force caused by the electric field. The responding movements depend on, besides the field strength, the inertial properties, damping factors like viscosity and collision frequencies and restoring factors i.e. factors tending to restore the equilibrium of the species in the material.

A fundamental and illustrating example is the Debye response, which describes non-interacting dipoles moving freely in a liquid. Exposed to an external ac voltage of angular frequency ω, the dipoles will cause a response, which gives the permittivity.

\[
\varepsilon_{\text{dipole}}^* = \varepsilon_{\text{hf}}' + \frac{\Delta \varepsilon'}{1 + j \omega \tau} = \varepsilon_{\text{hf}}' + \frac{\Delta \varepsilon'}{1 + (\omega \tau)^2} - j \frac{\Delta \varepsilon' \omega \tau}{1 + (\omega \tau)^2}
\]

where \( \Delta \varepsilon' \) reflects the number of dipoles and their dipole moment, \( \tau_v \) the relaxation time which is linked to damping effect of the viscosity of the medium surrounding the dipoles and \( \varepsilon_{\text{hf}} \) is the permittivity of the medium, [Jonscher (1983)]. In the real value permittivity (\( \varepsilon' \)) spectrum, this response recognizes as a step between the value \( \varepsilon_{\text{hf}} \) at high frequencies and the value \( \varepsilon_{\text{hf}} + \Delta \varepsilon \) at low frequencies. The slope of the step is -2 (logarithmic axes) and centres at the characteristic frequency \( 1/\tau_v \). In the imaginary value permittivity (\( \varepsilon'' \)) spectrum, this response recognizes as a peak at the characteristic frequency.

In more general cases the dipoles are not acting under such idealized circumstances, or characteristic parameters like \( \tau_v \) has a distribution, rather than having one distinct value. In these cases, modifications of the Debye response, e.g. Cole-Cole, Davidson-Cole and Havriliak-Negami responses may be useful. Furthermore other transport mechanisms, interfacial effects and electrochemical reactions give other types of responses, in different degrees reminding of the type given by eq.10 [Jonscher (1983)]. Various charged and dipolar species and other phenomena in a material and an experimental set-up, are each causing their specific features, superposing in the dielectric spectra.

In this thesis, free charges between blocking electrodes are studied, where the number of charge carriers and their mobility are of interest. Free charges between blocking electrodes cause a response (eq. 11) similar to the Debye response when exposed to an external voltage. As opposed to dipoles, how-
ever, the resulting permittivity is also dependent of the distance \((L_{el})\) between the electrodes [Schütts and Gerdes (1992a)]

\[
\varepsilon_{charge}^* = \varepsilon_{hf}^* + \frac{\delta \varepsilon_{hf}^*}{1 + (\delta \omega \tau)^2} - \frac{\int (\delta \omega \tau) \cdot \delta \varepsilon_{hf}^*}{1 + (\delta \omega \tau)^2}
\]

where \(\tau = \varepsilon_{hf}^* \sigma / \sigma\) is the electrical relaxation time of the system, \(\sigma\) is the conductivity, \(\delta = L_{el} / (2 \cdot \sqrt{D} \cdot \tau)\) and \(D\) is the diffusion coefficient.

To determine the number of free charge carriers \((n_0)\) in the sample, the following equation can be used [Schütts and Gerdes (1992b), Niklasson et al. (2005)].

\[
n_0 = \left(\frac{\sigma_{hf}^*}{\sqrt{(X - 1) \varepsilon_{hf}^* \omega \tau}}\right)^4 \frac{\varepsilon_{hf}^* kT}{Q^2 (L_{el} / 2)^2}
\]

where \(\sigma_{hf}^*\) is the conductivity in the high frequency region in which the real part of the permittivity equals \(\varepsilon_{hf}^*\), \(kT\) is the thermal energy, \(n_0\) and \(Q\) are the number of mobile charge carriers and their charge and \(X\) is any real number for which the relation \(\varepsilon'(\omega X) = X \varepsilon_{hf}^*\) is valid. Thus the choice of \(X\) determines \(\omega X\) or \(vice versa\). Equation 12 is derived from the real part of eq. 11 under the condition \((\delta \tau \cdot \omega)^2 / X^2 \gg 1\). Knowing both \(n_0\) and \(\sigma_{hf}^*\), the mobility \((\mu)\) and the diffusion coefficient \((D)\) of the charge carriers are readily obtained from the Nernst-Einstein relation:

\[
\mu = \frac{QD}{kT} = \frac{\sigma_{hf}^*}{n_0 Q}
\]

4.3.2 Description of the dielectric spectroscopy experiments

The sample was mounted between two planar gold plated brass electrodes, each with an area of 0.785 cm\(^2\). The electrodes were surrounded by a guard ring, and a guard circuit to provide a homogeneous electric field in the part of the sample measured. The guard electrode set-up required that the guard ring was insulated from one of the measuring electrodes. The electrode separation was set by a micrometer screw (fig 19). The entire electrode arrangement was embraced by a sealed stainless steel container in order to provide an electrically shielded environment [Welch (2006)]. A 100% relative humidity environment inside the container was ensured by adding water at the bottom of the stainless steel container. The temperatures were set and maintained by placing the electrode containing stainless steel container in an incubator
The LFDS measurements were carried out with a Novocontrol Alpha-AN dielectric measurement system (Novocontrol Technologies GmbH & Co. KG). Sinusoidal ac voltages were applied across the sample and the frequency of the voltage was scanned in logarithmically equal steps from the MHz to the sub mHz region. The responding current amplitude and phase were measured and analyzed and the real and imaginary parts of the permittivity were obtained as a function of the frequency.

4.4 X-ray crystallography

4.4.1 Theory of X-ray crystallography

X-ray crystallography relies on electromagnetic waves interacting with electrons of atoms and molecules. The electrons of a molecule exposed to electromagnetic radiation at the energies used (8.0 keV, $\lambda = 1.542$ Å), will, with good approximation, act as a diffuse Thompson scatterer [Ladd and Palmer (2003)]. Exposing molecules or molecular clusters such as micelles arranged in regular lattices (crystal or crystal-like) to electromagnetic radiation, the scattered radiation will by interference form diffraction patterns significant for the lattice pattern.

![Bragg reflection in crystal lattice. There will be constructive interference at exit angles where the Bragg condition fulfilled. Different crystal planes (Bragg planes) are indicated by dashed lines.](image)

More in detail, the diffraction pattern depends on crystal planes that appear in the structure. Depending on their angle towards the incoming beam, an angle-dependent spectrum will appear, where the intensities of the peaks, corresponding to specific crystal planes, reflect the number of scatterer and electron densities in those planes. According to Bragg’s law, constructive interference is obtained when...
where $d$ is the lattice spacing, $h$, $k$, $l$ are the Miller indices of the reflecting planes $\theta$ is the angle between the plane and the incident beam (as well as the angle between the plane and the scattered beam), $m$ is an integer (order of reflection) and $\lambda$ is the wavelength of the radiation [Ladd and Palmer (2003)].

4.4.2 Description of the small angle X-ray scattering experiments

Due to the rather big lattice spacing (some nm) in the gel samples, small angle X-ray scattering (SAXS) was appropriate for the determination of the gel lattice structure. The SAXS measurements were performed, using a Kratky camera with line collimation. The gel was cut to suitable size and mounted in a vacuum-sealed sample holder. Cu K$\alpha$ radiation of $\lambda = 1.542 \text{ Å}$ was provided by a Seifert Iso-Debyeflex 3003 generator working at 50 kV and 40 mA. A MBraun linear position sensitive detector PSD 50M was used to record the diffraction pattern. The sample was investigated at temperatures between room temperature and ~65 °C. Prior to measurement the sample was allowed to equilibrate at the new temperature for two hours.

4.5 Release modeling of binary surfactant gels

A mixture of different surfactants in aqueous solution may also result in a micelle system. Modelling the surfactant release from such a system in contact with another system, e.g. a water bath, the thermodynamic equilibrium between the surfactants as monomer and as incorporated in micelles is a crucial part

4.5.1 Theory

4.5.1.1 Thermodynamic equilibrium conditions

The system is approximated as a separated two-phase system, where one phase is the aqueous monomer solution and the other phase is representing the micelles as one continuous non-aqueous binary mixture of surfactants. Here, the latter phase is approximated as a regular solution. This means that in the thermodynamic treatment, the entropy of surfactant mixing is considered - as in the ideal solution model - but also the difference in energy ($W$) in interaction between like and unlike surfactants. In this model the entropy of
mixing of whole micelles in the whole system is neglected [Holland and Rubingh (1983)].

For such a system the following relation is valid [Holland and Rubingh (1983)]:

\[ C_i = f_i x_i CMC_i \quad i=1,2 \quad \text{eq. 15} \]

where \( C_i \) is the monomer concentration of surfactant \( i \), \( x_i \) is the molar fraction of surfactant \( i \) in the micelles, \( CMC_i \) is the critical micelle concentration for surfactant \( i \), and \( f_i \) the activity coefficient, which according to the regular solution model is calculated as

\[ f_i = e^{\beta (1-x_i)^2} \quad \text{eq. 16} \]

where \( \beta = W/RT \).

The binary system will have a CMC value (\( CMC_{mix} \)) leading to the following relations:

\[ C_i = CMC_{mix} \cdot \alpha_i \quad \text{eq. 17} \]

and

\[ \frac{1}{CMC_{mix}} = \frac{\alpha_i}{f_i C_1} + \frac{\alpha_2}{f_2 C_2} \quad \text{eq. 18} \]

where \( \alpha_i \) is the total molar fraction of surfactant \( i \). From these relations and the constraint \( x_1 + x_2 = 1 \), \( CMC_{mix} \) can be determined. Finally, the following relation must be valid:

\[ x_i = \frac{C_i^{\text{tot}} - C_i}{C_i^{\text{tot}} - C_1 - C_2} \quad \text{eq. 19} \]

where \( C_i^{\text{tot}} \) is the total concentration of surfactant \( i \) and \( C_i^{\text{tot}} \) is the sum concentration of surfactant species 1 and 2.

**4.5.1.2 Release from a micelle solution across a membrane**

The transport from a micelle solution across a membrane (fig. 21 A and C) is described by Fick’s first law:
\[- \frac{\partial C_i^{\text{tot}}}{\partial t} = \frac{A_{\text{mem}} \cdot D_i}{V_{\text{sol}}} \frac{\partial C_i}{\partial x} \approx \frac{A_{\text{mem}} \cdot D_i}{V_{\text{sol}} \cdot h_{\text{mem}}} C_i \]  

\text{eq. 20}

where \( D_i \) is the diffusion coefficient of surfactant \( i \), \( V_{\text{sol}} \) is the volume of the micelle solution and \( A_{\text{mem}} \) and \( h_{\text{mem}} \) is the cross sectional area and thickness of the membrane respectively. Assuming that no micelle can transport across the membrane, the transport rate (middle part of eq. 20) is determined by the gradient of the monomer concentration, \( C_i \), while the concentration rate change (left part of eq. 20) must concern the total concentration. Assuming steady state and sink condition, i.e. practically zero concentration, on the receiver side, the last equality is obtained.

4.5.1.3 Release from a micelle solution in a gel matrix

In this type of experiment, (see below) the micelle solution is embedded in a slab-formed gel matrix, where one of the slab surfaces is in contact with an aqueous receiver, under sink condition, and the others to impermeable walls. Under such circumstances, the gel will consist, depending on local monomer concentrations and resulting \( CMC_{\text{mix}} \), of one phase with micelles and monomers and one phase of only monomers (fig. 21 B and D). Due to the depletion of surfactants in the system with time, the micelle free phase will grow and consequently, the micelle containing phase will shrink. The transport- and concentration changes in the system are described by Fick’s second law:

\[ D_i \frac{\partial^2 C_i}{\partial x^2} = \frac{\partial C_i^{\text{tot}}}{\partial t} \]  

\text{eq. 21}

Assuming that no micelle can migrate in the gel matrix, the transport rate on the left part is determined by the Laplacian of the monomer fraction \( C_i \), while the concentration rate change given on the right hand side of the equation must concern the total concentration.

4.5.1.4 The heat balance integral method

The heat balance integral method can be used to obtain simplified solutions of heat and transport equations of the Fickian type, like eq. 21 [Langford (1973), Goodman (1958)]. An Ansatz with a parameterized function is made as an approximate solution of the transport equation. In case of many phase systems, such as moving boundary systems, an Ansatz is done for every phase. The ruling transport equation is integrated over the entire phase, giving what is called the heat balance integral. This integral equation reduces the requirements of the solution function to the boundaries of the phase rather than the entire phase and can, therefore, be seen as a weaker form of transport equation. The parameters of the Ansatz function are then set by the
boundary conditions in terms of continuity and/or balance conditions across the boundaries.

Figure 21. Surfactant release experiments of a binary micelle solution through a membrane and a binary micelle polymer gel matrix. The upper panels show diagrams of typical concentration profiles in the surfactant solution and in the membrane (A) and in binary micelle polymer gel matrix (B). The lower panels show drawings of the experiment chambers for gel release experiment through membrane (C) and gel matrix (D).

4.5.2 Description of the release experiments

In the release experiments the gels and solutions were placed in specially built containers (fig. 21 C and D). The containers used for the solutions were covered with a dialysis membrane and were then filled through a small hole at the bottom of the container. In the gel experiments the samples were first
placed into the containers, whereupon they were covered with a coarse-size plastic net and a stainless steel net. The containers, in turn, were placed in an USP dissolution bath where the release medium was a 0.9% NaCl solution. The concentration of the released surfactants was analysed by continuously pumping the release medium through a spectrophotometer.
5 Preparations of samples

5.1 Gel samples
Dodecyltrimethylammonium hydroxide (DoTAOH) was prepared [Norrman et al. (2007)] by dissolving 10 g Dodecyltrimethylammonium bromide (DoTAB) in a plastic beaker containing 100 to 150 g of anion exchange resin (Dowex) and 150 ml Millipore water. The solution was stirred for two hours and then vacuum filtered. The resin was then rinsed with an additional 50-75 ml millipore water and vacuum filtered to extract any remaining DoTAOH. Fresh Dowex (100 to 150 g) was added to the filtrate and the procedure was repeated 3 times to ensure a low content of Br⁻ ions in the final product. The final solution was then frozen and freeze-dried for a few days. After freeze drying, the powder was quickly transferred into a sealed container avoiding wetting of the highly hygroscopic powder. Dowex was charged with hydroxide ions by stirring with 1M NaOH solution (4-5 times more ion equivalents [Göransson and Hansson (2003), Nilsson and Hansson (2005)].

A polyacrylic gel was prepared by mixing a solution (around 40 ml) of 1.75 M (5.10 g) acrylic acid, 15 mM (0.097 g) NMBA (crosslinker), 6 mM TEMED (accelerator) and 6 mM AP (initiator). The solution was transferred into glass tubes (about 10 cm length, diameter 17 mm, one end capped) and heated to 65 °C for 12 hours. The polymer gels were removed from the tubes and washed (3 × 12 hours) with large excesses of water.

To prepare a Dodecyltrimethylammonium/polyacrylate (DoTAPA) gel, the polymer gel was cut into 1-2 mm thick disks, put into test tubes and weighed. A reference piece of polymer was weighed in wet state and after 4 days of freeze drying. The dry/wet ratio was used to calculate molar content of COO⁻ in each piece. In the calculations compensation for the sites where crosslinking agent had replaced a COO⁻ group was made. A stock solution of approximately 0.1 M DoTAOH was prepared. The mole DoTAOH to weighed solution ratio of the stock solution was calculated. For each test tube the same mole of DoTAOH as molar content of COO⁻ in the polymer gel, was added by weighing the added solution. The gel was left for 3 weeks to equilibrate.

The Dodecyltrimethylammonium chloride (DoTAC) gel was prepared by mixing an equal weight of DoTAC and water. Then, after mounting the sample in the flow cell, the desired humidity was then set after mounting the
sample in the flow cell, by flowing the cell of He or N₂ gas at appropriate % RH.

5.2 Solutions
Aqueous 0.48 M glycine solutions were prepared with pH-values of 1, 6, and 12, at which one specific ionic form of glycine is completely dominating. The intermediate pH was obtained by dissolving glycine in water, whereas high and low pHs were set by adding 0.48 M(aq) of NaOH or 0.56 M(aq) of HCl to the glycine solution. The pH was monitored by indicator paper with a resolution of 0.3 pH units. Sodium polyacrylate was prepared in 0.3 M water solution.
6 Results

First a summary is presented from three works based on RIXS and XAS measurements on pure water, on DoTAC gel systems (confined water) and glycine and sodium polyacrylate (Paper I, II and III). Secondly a summary is given of dielectric spectroscopy results and X-ray crystallography measurements in a surfactant – poly-ion (dodecyltrimethylammonium – polyacrylate (DoTAPA)) complex, in which the relation between structure and mobility is determined (Paper IV and V). Finally the results from the developed surfactant release models are summarized. The models are applied to mixed cat-anionic (Tetracaine – SDS and Diphenhydramine – SDS) surfactant micelle liquid crystal systems. Validation of the models has been done by comparing outcome of the model to experimental release data (Paper VI and VII).

6.1 The soft X-ray spectroscopy measurements (Paper I –III)

The X-ray emission spectra of gas-phase water is dominated by three distinct features [Rubensson et al. (1985), Nordgren et al. (1975), Gilberg et al. (1982)]. These have been assigned to final states with vacancies in the valence orbitals denoted 1b₂, 3a₁ and 1b₁, according to their symmetry in the C₂ᵥ point group of the water molecule. In liquid water the three features remain, although energetically shifted, and broadened [Guo et al. (2002)] and the 1b₂, 3a₁, 1b₁ notation has remained also for liquid water in the literature (fig. 22).

The 1b₁ feature in water has later [Fuchs et al. (2008)] been shown to have an internal double peak structure, where the peaks are denoted d₁ (high energy) and d₂ (low energy) respectively (fig. 23). The interpretation of this double peak in the RIXS spectra has been lively debated [Fuchs et al. (2008), Tokushima et al. (2008), Odelius (2009), Nilsson and Pettersson (2011), Tokushima et al. (2012)].

The XAS spectrum of liquid water shows a main edge at 537.5 eV and a pre-peak at 534.7 eV (fig. 23). Also for the XAS features the orbitals for an isolated molecule are taken as starting point. Thus, the pre-peak can be associated with excitation into the first unoccupied orbital, 4a₁, [Wang et al. (2006), Weinhardt et al. (2012)] and the main edge structure, with excitation
into the second unoccupied orbital, 2b₂ [Weinhardt et al. (2012), Myeni et al. (2002), Wang et al. (2006)]. From the spectra it is obvious that the influence of the neighbouring molecules is large, and the interpretation is also under debate.

![Graph showing energy vs. intensity for water molecule and liquid water](image)

Figure 22. Measured and simulated RIXS spectra of gas phase and bulk water (from Guo et al. (2002)).

Measuring on carboxylic acids in aqueous solution at the O K-edge, the spectral contribution from water molecules are interfering with O K-edge spectra of the carboxylate/carboxylic groups. For the -OH group in the carboxylic group the resonance feature coincides with OH bond resonance feature of water at ~534 eV [Tokushima et al. (2009)]. For the carbonyl group and the resonance structure in the carboxylate group, however, the absorption resonances occur below that energy [Tokushima et al. (2009)]. XAS features observed in this lower energy range could therefore be assigned to these groups and site-selective excitation in the RIXS measurements could thus be accomplished.

6.1.1 Measurements on bulk water (Paper I)

In RIXS, the emitted radiation has angular anisotropy, due to the polarization of the exciting radiation and the symmetry of the orbitals involved in the excitation-deexcitation process [Mayer et al (1991), Kashtanov et al. (2004),]
Luo et al. (1996). For resonances involving a symmetric 1s core level, the phenomenology becomes particularly simple: one expects relative attenuation of the emission in directions parallel to the polarization direction when the orbital populated in the first step of the scattering process has the same symmetry as the orbital depopulated in the second step. Conversely, an enhancement is expected when the directions are perpendicular. Thus, the angular distribution can be essential when assigning the spectral features.

In paper I emission spectra from pure water have been measured in the direction parallel and inclined 65° (here called perpendicular) to the polarization direction of the exciting radiation. The $a_1$, $b_1$ and $b_2$ symmetry assignments for the valence orbitals of the free molecule are not strictly valid for the unordered liquid. We expect distortion of the symmetries induced by interaction in the liquid, due to the hydrogen bonds and therefore also changes in the angular anisotropy in RIXS measurements. We indeed observe an angular anisotropy in the RIXS measurements, and it is much less pronounced than what is predicted for the free molecule [Luo et al. (1996), Kashtanov et al. (2004)]

![Image](image1)

*Figure 23.* Measured RIXS and XAS spectra (here denoted SXE and SXA) of bulk water in parallel and “perpendicular” direction relative the polarization direction.

In RIXS measured at the pre-peak, the observed attenuation in parallel direction of the feature attributed to the $3a_1$ orbital is thus in line with excitation to the $4a_1$ orbital. It can also be noted that the elastic peak and especially the
loss tail show this behaviour. This is expected as this intensity corresponds to recombination, where the initially excited electron fills the core hole in the second step. The loss tail and the smearing out of the features indicate a substantial nuclear rearrangement. In the gas phase ultrafast dissociation is observed for excitation to the 4a_1 orbital (fig. 23).

In RIXS measured at the main edge, the d_1 and d_2 features show different attenuation/enhancement behaviour, suggesting that the orbital giving the d_1 feature has a more b_1 like symmetry than the orbital giving the d_2 feature (fig. 23). This is consistent with attributing the d_1 peak to the non hydrogen bonding free electron pair supposed to have b_1 symmetry and the d_2 peak to hydrogen bonding of that orbital [Tokushima et al. (2008)], then obtaining a less b_1 character, but it is also consistent with attributing the d_2 peak to a dissociated molecule [Fuchs et al. (2008)], also leading to an orbital of less b_1 character.

6.1.2 Measurements on water confined in a surfactant gel (Paper II)

In Paper II, soft X-ray spectroscopy at the oxygen K-edge has been performed on DoTAC gels with varying water content. Because only the water molecules in the systems contain oxygen atoms, soft X-ray spectroscopy could be used to selectively study the water molecules and their interaction with the surrounding.

No dramatic differences between XAS spectra of the gel and bulk water spectra are observed. In RIXS spectra, however, pronounced differences are noted between bulk water and water confined in the micelle lattice (fig. 24). The spectra are compared to simulated spectra of a water molecule in various environments, (fig. 25) investigating the effect of the interaction between the trimethylammonium group and water, and between the chlorine ion and water, in order to mimic the confined intermicellar water. It can be concluded that this relatively simple model, to a large extent, explains the differences in the measured surfactant gel spectra compared to bulk water spectra.

In RIXS spectra excited at the main edge, the features are essentially the same as in spectra of bulk water (fig. 24), i.e. corresponding to the water orbitals 1b_2, 3a_1 (bonding) and 1b_1 (lone pair) orbitals. In the measured spectra, however, a decreased energy difference between the 1b_2 and 1b_1 features by 1.2 eV compared to gas phase water is noted. This trend is seen in simulated spectra by a decreased energy difference of 0.7 eV.

The 1b_1 feature in the measured spectra is narrower than in bulk water. The remaining high-energy flank of the 1b_1 feature, may be interpreted as a remaining, highly suppressed d_1 feature. A water-content dependent difference in intensity of this flank feature is also observed. The interpretation of
This phenomenon depends on the assignment of the double structure in bulk water. [Fuchs et al. (2008), Tokushima et al. (2008)] but in both views the high-energy partner corresponds to less interaction with the surrounding. This is in line with our observation and the fact that the interaction is strong in the present case.

![Graph](image)

Figure 24. Measured RIXS spectra (here denoted SXE) of bulk water and micelle confined water. Oxygen K-edge spectra of DoTAC gel with 25 wt % (green) and 10 wt % (red) water. The FY spectra are shown in the upper right, and the excitation energies used for the RIXS spectra are indicated. The spectra of bulk liquid water (blue) are shown for comparison.

Also the $3a_1$ feature in the measured spectra from the micelle systems is narrower, suggesting that the water molecules here are more stabilized towards nuclear rearrangement than in bulk water.

In RIXS spectra excited at the prepeak, the $3a_1$ and $1b_2$ features are smeared out, comparing to the main peak spectra, something that is also observed in bulk water spectra (fig 24). Notably the $1b_1$ feature has an extra broadening towards lower energies compared to the $1b_1$ feature of bulk water. For the off-resonance excitation, the width of the $1b_1$ feature is also dependent on the water concentration.

Nuclear motion might also be the cause of the general energy broadening of the features from the de-excitation of the $1b_2$, $3a_1$ and $1b_1$ orbitals. The extra broadening of the $1b_1$ feature may be attributed to an effect of an ensemble of non-equivalent sites. Following the predictions by the model cal-
calculations, we assign the structure on the high-energy side of the 1b₁ peak to hybridization between Cl⁻ 3p and H₂O 1b₁ states.

Figure 25. Simulated RIXS spectra for different configuration of micelle confined water. Predicted RIXS spectra for (A) a single water molecule, (B) water with a tetramethylammonium ion as neighbour, (C) with a chlorine ion as neighbour, and (D) with both ions. The nuclear positions are optimized for the latter configuration. Electron density plots are included to show the orbitals corresponding to the three contributing valence orbitals in the water molecule (above) and to some representative orbitals in the complex with surrounding ions (below). The faint low energy feature below 1b₂ in the measured spectra has a counterpart in the simulated spectra and is by calculations assigned to states of primarily Cl⁻ 3s character mixed with water 1b₂ character. Interestingly, this feature does not appear in water interacting solely with chlorine ion, but require the presence of the trimethylammonium group.

6.1.3 Measurements on carboxylic acids (Paper III)

Paper III focuses on carboxylic/carboxylate groups and amine groups. XAS and RIXS measurements were performed at the O and N K-edges on aqueous solutions of glycine, and poly-ionic sodium polyacrylate i.e. the sodium salt of polyacrylic acid.

For glycine solution, measurements were carried out at three different pH. Thereby, the effects of protonation on the amine group as well as deprotonation of the carboxyl group on the local electronic structure were determined. At pH 1, an overwhelming majority of the molecules have protonized amine
groups and neutral carboxyl groups, at pH 6, an overwhelming majority of the molecules have protonized amine groups and deprotonized carboxyl groups and at pH 12, an overwhelming majority of the molecules have neutral amine groups and deprotonized carboxyl group. For comparison O K-edge spectra of sodium polyacrylate - where the carboxylate groups are deprotonized - have been measured (fig.26).

Figure 26. (A) Oxygen K-edge XAS and RIXS (here denoted SXE and SXA) spectra of glycine in water solution at pH 1 and pH 6. Oxygen K emission spectra of glycine in water solution at pH 1 (black) and pH 6 (red). Above 534 eV, the absorption in water dominates the SXA spectrum, and the SXE spectra excited at higher energies are identical to the spectra of pure water (blue dots) within our experimental accuracy. Spectra excited at the resonance around 532-533 eV can be associated with excitations localized at the oxygen atom at the –C=O group of glycine. The absorption spectrum in the inset is not corrected for self-absorption. (B) Oxygen K XAS and RIXS spectra of glycine at pH 6 (red) and sodium poly acrylate (blue). In both systems, the carboxylic group takes the –COO⁻ form.

The Oxygen XAS spectra above 534 eV are practically identical to that of pure water (fig. 26) and it is assigned accordingly. Below this region a peak at 532-533 eV is observed which is not present in pure water. In this region the structure is assigned to the carboxylic/carboxylate group [Cannington and Ham (1983) Messer et al. (2005), Plekan et al. (2007a)]. The energy of this peak is almost identical for the glycine at pH 6 and sodium polycrylate while a clear energy difference of 0.4 eV for glycine solution at pH 1 is observed.

Also in the oxygen RIXS measurements, the spectra measured on glycine at pH 6 and sodium polycrylate show similar features, while the spectrum measured on glycine at pH 1 show clear differences (fig 26). Still, looking at the finer details, differences are noted between sodium polyacrylate and glycine spectra and this might be associated with different pKₐ of the carboxylate groups in the two compounds.
In summary, the spectra associated with the carboxylic groups show similar features, largely independent of the host molecule, but on the other hand, the spectra are very sensitive to deprotonation: the groups, including their protonation state leave distinct fingerprints in the data. Similar conclusions can be made for the corresponding spectra at the nitrogen K-edge, which are sensitive to the protonation of the amine group (fig.27). The physics reflected in the spectral behaviour is discussed in terms of published results [Cannington and Ham (1983), Gordon et al. (2003), Messer et al. (2005), Plekan et al. (2007a), Plekan et al. (2007b), Tokushima et al. (2009)].

**Figure 27.** Nitrogen K-edge XAS and RIXS spectra (here denoted SXE and SXA) of glycine at pH 6 (blue) and pH 12 (red).

6.2 Mobility structure relationship of Dodecyltrimethylammonium /Polyacrylic composite gel (Paper IV and V)

In a DoTAPA composite gel, the mobility of the monomer fraction of the surfactant was investigated, with focus on the dependence on the liquid crystal structure. A stoichiometrically balanced DoTAPA gel was prepared in order to minimize the amount of free small ion species (OH\(^-\), H\(^+\)) in advance for monomere DoTA\(^+\)-ions. Dielectric spectra were recorded by the LFDS technique at different temperature in the 22.3- 65 °C interval and the liquid crystal structures in the same temperature interval were determined, by SAXS.

Using eq. 12 the mobility and number of mobile surfactant ions could be determined from the imaginary and real parts of the recorded spectra. In this study, the extraction of the \(\varepsilon'_{hf}\) -value was a challenge due to obscuring features from higher frequency processes. A method to determine \(\varepsilon'_{hf}\) under
such circumstances, by recording spectra at difference electrode separations was developed in Paper V. The method relies on the following equation:

\[
\epsilon'_{hf} = \frac{\epsilon'_1(\omega) \cdot L_1 - \epsilon'_2(\omega) \cdot L_2}{L_1 - L_2}
\]

where \( \epsilon'_1(\omega) \) and \( \epsilon'_2(\omega) \) are the real parts of the permittivity measured at the angular frequency \( \omega \) and at electrode separations \( L_1 \) and \( L_2 \). The method was evaluated by applying it on dielectric spectra measured on an ion conducting cellulose gel biosynthesized by the \textit{Acetobacter xylinum} bacterium. The obtained \( \epsilon'_{hf} \) value showed good accordance with an earlier study [Gelin \textit{et al.} (2007)] of that cellulose gel, where \( \epsilon'_{hf} \) also could be determined in a conventional way by an unobstructed high frequency plateau.

The mobility analysis show a strong positive correlation between temperature and mobility as well as a strong negative correlation between temperature and number of mobile charge carriers (fig. 28).

![Figure 28](image)

\textit{Figure 28.} Charge carrier concentration \( n_0 \) (A) and diffusion coefficient \( D \) (B) as functions of the inverse thermal energy as extracted from LFDS spectra. The error bars represent the total deviation over three separate extractions.

The SAXS measurements show a gradual change from a predominance of domains of orthorombically hexagonally close packed (HCP) spherical or spheroid micelles at the lower temperatures to a predominance of domains of hexagonally arranged rod-shaped cylindrical micelles at the higher temperatures (fig. 29). Thus, the increase of mobility at higher temperature is correlated with the increased fraction of rod shaped micelles.

This finding is also consistent with earlier observations. In poly-ion gels surrounded by surfactant solutions, the growth rate of the surfactant/poly-ion complex shell is dependent of the microstructure of the shell. This can be seen as indirect observations of transport rate connected to the liquid crystal structure [Nilsson and Hansson (2008), Göransson and Hansson (2003)].
An explanation of the structure correlated transport rate is suggested, where, by a residence-time hopping mechanism, the rod shaped micelles mediate the transport of monomers more efficiently than the spherical micelles.

![Graph](image)

Figure 29. SAXS spectra recorded of the gel complex. At 25 °C the sample entirely consists of HCP arranged micelles, while at 65 °C the sample entirely consists of hexagonal phase micelles. The two vertical dotted lines indicate the position of the main feature of HCP (left) and hexagonal phase (right). Noticeable are the gradual relative increase of the hexagonal peak with temperature and the gradual relative decrease of the HCP peak.

6.3 Development of a model for surfactant release in a binary surfactant system (Paper VI and VII)

In this work models were developed for transport and release of the surfactant components from binary catanionic surfactant micelle gel systems. The accuracy of the models was investigated by comparison with experimental data.

The models considered the thermodynamic equilibrium between the monomer concentration and the proportions of cationic and anionic surfactants in the micelles. This is quantitatively described by eqs. 15-19. Further, Fick’s first (eq. 20) and second laws (eq. 21), respectively, were applied when modelling release from a solution across a membrane and transport out of a gel matrix.

The transport (diffusion) through the membrane and release were quantified by numerical solution (Runge - Kutta) of the ordinary differential equation (eq. 20) linked to a numerical solution of the monomer - micelle surfactant equilibrium described by eqs. 15 - 19. Experimentally and theoretically
generated data were compared for different parameter sets. The theoretical release profiles show a good concordance with experimental data (fig. 30).

Figure 30. The release profiles from (A) 14mM diphenhydramine/26mM SDS vesicle solution and (B) 8mM diphenhydramine/32mM SDS micellar solution through a dialysis membrane. Symbols are experimental points for diphenhydramine (black) and SDS (gray). The standard deviation is given for each measured value. The lines indicate the theoretical predictions for the interaction parameter $\beta = -8.4$, and colored grey and black correspondingly to the measured data.

To quantify the transport and release out of a gel matrix, eq. 21 was first rewritten in terms of free monomer ($C_i$) and micelle bound ($S_i$) concentrations, giving:

$$D_i \frac{\partial^2 C_i}{\partial x^2} = \frac{\partial C_i}{\partial t} + \frac{\partial S_i}{\partial t} \quad \text{eq. 23}$$

Equation 23 was solved with aid of the Finite Element Method (FEM), considering the equilibrium conditions between the $S_i$ and $C_i$, by eqs. 15 – 19. The obtained release profiles show good agreement with experimental values validating the proposed model (fig 31).

Implementing FEM is, however demanding and therefore an approximate solution method, simplifying the mathematical treatment, is desirable. By a Boltzmann-transformation, [Crank (1957)], i.e. introducing the variable $\eta$ such: $\eta = x / 2 \sqrt{t}$, eq. 23 was transformed into an ordinary differential equation.

$$D_i \frac{d^2 C_i}{d \eta^2} + 2 \eta \cdot \left( \frac{d C_i}{d \eta} + \frac{d S_i}{d \eta} \right) = 0 \quad \text{eq. 24}$$

This required that one could approximate the gel as semi-infinite, i.e. that the impermeable wall is sufficiently far away, so that it does not influence the release at the front. Already here the problem was simplified by the far more
easily implemented and less time consuming procedure of solving an ordinary differential equation.

Figure 31. The release profiles of a (A) 14mM tetracaine and 26mM SDS vesicle composition and a (B) 26mM tetracaine and 14mM SDS vesicle composition from 1% C940 gels, where the symbols denote measured levels of tetracaine (black) and SDS (gray). The standard deviation is given for each measured value. Modelled profiles are shown as lines, colored corresponding to the measured data.

Using the pseudo-steady-state approximation and the heat balance integral method [Langford (1973), Goodman (1958)], the problem was transformed into a non-linear equation system with four equations. One of the equations had to be solved numerically whereupon the other equations could be solved analytically. Thus, the original model requiring FEM had, by some modest simplifications, been transformed into the much simpler problem of numerically solving an equation.

Figure 32. Comparison between numerically and analytically determined release constants for (A) the slab geometry and (B) the half infinite geometry.

To assess the simplified model, the obtained release rates were compared to the release rates obtained from the more exact treatment of eq. 23 (requiring FEM). Comparisons were made at different levels of the CMC:s, the initial
concentrations and diffusion coefficients of surfactant interaction parameter, $\beta$. The approximation of infinite gel matrix was tested by comparing obtained values to the data from paper VI, where FEM solution of eq. 23 was applied on a finite gel slab. In addition, the simplified treatment by the heat balance integral method was tested by comparing obtained values to values obtained from the solution of the ordinary differential equation of eq. 24. The obtained release rates show a good accordance between the models in the selected range of parameters (fig. 32).

6.4 Results summarized

- It is possible to perform XAS and RIXS measurements in gel systems (confined water) and to map out the molecule configuration in such systems as well as studying the electronic structure of confined water.

- The XAS and RIXS measurements on molecules containing amine and carboxyl groups showed a strong influence of protonization/ deprotonization on spectra as well as minor spectral differences between different carboxylic acids, maybe reflecting different pKa.

- By dielectric spectroscopy, the surfactant mobility in micelle/poly-ion gel system was determined. Also, a relation was found between the apparent mobility and the liquid crystalline structure in the micelle poly-ion gel system.

- The release of surfactant components in binary surfactant micelle gel systems was modeled and the model was verified experimentally. The model makes it possible to relate the system specific transport-, interaction- composition- and chemical equilibrium parameters to the release rate in such systems. This model has also, by approximations, been simplified mathematically, which considerably reduced the required CPU time in the calculations. Furthermore, this simplification has lowered the required mathematical/programming expertise level when setting up calculations on analogue systems and thus making the model more accessible for larger groups of researchers.

- The liquid flow system and humidity flow system have been improved.
7 Outlook and Future

7.1 Gel complexes
The soft X–ray spectroscopy gel study has demonstrated the strong influence of the chemical surrounding on the water molecule. This suggests for making follow-up studies on surfactant/polyion complexes, e.g. of the carbon in the trimethylammonium groups and oxygen in the carboxylate groups of the polyacrylate. In such studies long chained cross-linked poly-ions should be avoided because of its more static behavior and the risk for X-ray induced decomposition of the sample. Shorter one-dimensional acrylate-chains are more mobile, and a high exchange rate of polyacrylate molecules in the X-ray exposed part of the sample is expected. Thereby the risk for radiation damage on the polymer chains will diminish. To facilitate the analysis of these measurements, reference studies on tetramethylammonium-ions in water and on aliphatic hydrocarbons should also be performed. By such studies, spectral features originating from the carbon chains in the interior of micelles could be identified.

7.2 Confined water
In order to deepen the understanding of bulk water as well as the understanding of water behavior under confined circumstances, further studies of confined water could be conducted. Clays and different types of micelle- or inverted micelle systems could be used to obtain such confinements. Clays such as montmorillonite and kaolinite have direct applications, e.g. for encapsulation of nuclear waste, as stabilizer in pharmaceutical formulations, as formulation matrix for controlled release of drugs and as construction materials. Water appears confined in other natural systems such as biological cells. Micelle or inverted micelle systems could, therefore, possibly mimic cells in that aspect.

7.3 Carboxylic acids
The carboxyl study has shown detectable spectral differences between different carboxylic acids and could therefore be seen as the first step of a lar-
ger detailed investigation. By studying homological series of organic acids and amino acids it might be possible to understand the mechanisms for protonization and deprotonization in detail, and thereby the factors determining the pKₐ.

7.4 Development potential of the humidity and liquid flow system

The humidity system is quite stable. However, the humidity is not automatically regulated but controlled by a set duty cycle of switching between dry and humid gas and the flow (inlet pressure) of the gas. It is not trivial to make the correct setting, and it also requires that the humidity has to be monitored manually. Developing a reliable regulated system would be an improvement. The present system can reach a maximum humidity of 90 %RH in the sample cell. This is due to the pressure drop in the relatively long and narrow tubes between humidity switch and the sample cell. If shorter and/or wider tubes could be used, humidity close to 100 % could be achieved. The sample change procedure is also rather time consuming and developing a system for faster sample changes would be desirable.

7.5 Dielectric measurements

By measuring on samples with different contents of small ions, e.g. H⁺, OH⁻ and Cl⁻, their role in the dielectric spectra might be determined. Further composite gel systems containing surfactants with different mobility and monomer concentration could be measured both to characterize these system but also to further verify the already obtained results. Since only the cubic phase was present at 22 °C and at temperatures below, a mobility study by dielectric spectroscopy in the temperature region between 0 °C and 22 °C could be of interest and, according to the suggested model, expected to show a weaker temperature dependence than the one observed in these studies.

Due to the different coexisting crystalline micelle phases it is reasonable to assume that the mobility of the surfactants is distributed rather than taking one distinct value. Furthermore, when rod-like micelles are present in the sample, it is reasonable to assume a distribution of the surfactant mobilities also due to the distribution of the micelle orientation relative the applied electric field in the measurements. A more quantitative model could be developed by considering these effects.
7.6 Modeling of surfactant transport and gel-complex formation

Results, thinking and solving techniques from the release modelling could be applied to ion gel formation modelling. The formation process of a gel complex, i.e. surfactants migrating into a gel matrix and there forming micelles, could be seen as a reverted release process. In this modelling it is essential to know the monomer fraction and diffusion coefficients of the surfactants as well as the structure and configuration on the molecular level of the aqueous phase in the intermicelle region.
I den här avhandlingen presenteras resultat och slutsatser från studier av vatten, blandningar av vatten och organiska syror och blandningar av vatten och så kallade surfaktanter.

Vatten är utan tvekan ett av de viktigaste kemiska ämnena i våra liv. Vi består i huvudsak av vatten, det ingår i de biologiska processer som håller oss vid liv och det vi äter - i huvudsak växter och djur - är i likhet med oss själva också till stor del bestående och beroende av vatten. Vatten finns också i vår omgivning i form av atmosfärens vattenånga, mark- och grundvatten, sjöar, vattendrag, hav och isar och det förekommer också som en viktig beståndsdel i olika industriprocesser. Många forskare och forskargrupper ägnar sig åt att studera vatten ur olika aspekter och i olika sammanhang. Trots mycken forskarmöda och vattenmolekylens enkla struktur, återstår en hel del oklarheter om vattens natur och i vetenskapssammanhang är diskussionen livlig.

En organisk syra utmärks av att molekylen innehåller minst en s.k. karboxylgrupp. Denna kan i vattenlösning lämna ifrån sig en vätejon (deproto- niseras) och syrans styrka är beroende på hur hårt vätet är bundet till karboxylgruppen. Organiska syror ingår t.ex. i DNA, i proteiner som aminosyror och i olika kroppssjuka processer.

8.1 Studier av elektronstruktur i vatten, lösningar med organiska syror och micellsystem

I tre av avhandlingens arbeten används två besläktade experimentella metoder; röntgenabsorptionsspektroskopi och röntgenemissionsspektroskopi. För att förstå dessa arbeten underlättar det om man har lite översiktlig kunskap om atomers och molekylers uppbyggnad så väl som hur metoderna fungerar.


I röntgenabsorptionsspektroskopi bestrålas provet med röntgenstrålning som man låter variera inom ett energiintervall. Om röntgenstrålningens energi motsvarar energikillnaden mellan en besatt och en obesatt orbital för någon atom, kan en elektron hoppa (exciteras) från den besatta orbitalen (med lägre energi) till den obesatta orbitalen (med högre energi) och röntgenstrålningen kommer då att till viss del absorberas. Man noterar vid vilka energier på strålningen då absorptionen är hög och får därmed reda på energikillnaderna mellan några av de obesatta och besatta orbitalerna.


En fördel med dessa metoder är att man med lämpligt val av energiintervall på röntgenstrålningen kan styra vilket atomslag (t.ex. syre) man vill studera.

I två av de ovan nämnda avhandlingsarbetena studerades elektronstrukturer i vatten dels som ren substans och dels i ett micellsystem där den micellbildande surfaktanten var dodecytrimethylammoniumklorid. I det senare fallet så bildar dodecytrimethylammoniumjoner miceller medan vatten och kloridjoner bildar en slags lösning som omger micellerna.

Sådana här studier av vatten, rent eller i olika lösningar, har gjorts tidigare, men hur dessa ska tolkas i termer av elektronstruktur är fortfarande omdebatterat. I det första avhandlingsarbetet mättes röntgenemission i olika riktningar ut från provet. Ett riktningsberoende av emissionen är teoretiskt predikterat och beroende av elektronstrukturen. En sådan här studie kan alltså bidra till tolkningen av spektra i termer av elektronstruktur och i en vidare mening också hur vattenmolekyler arrangerar sig tillsammans. I det andra avhandlingsarbetet studerades vatten för att se hur det arrangerar sig tillsammans med miceller och kloridjoner. En jämförelse mellan de uppmätta spektra i detta arbete och spektra från rent vatten kan också vara användbara i tolkningen av de senare.

I det tredje avhandlingsarbetet studerades elektronstrukturen i vattenlösningar av aminosyran glycin och av natriumpolyakrylat. Genom att ställa pH (surhetsgraden) på glycinlösningen kan man styra ifall karboxylgruppen ska ha kvar vätejonen eller vara deprotoniserad. Här undersöktes skillnaderna i spektra och elektronstrukturen mellan deprotoniserad och icke deprotoniserad karboxylgrupp. I spektra konstaterades tydliga skillnader, som tolkades i termer av elektronstruktur. I den andra substansen, natriumpolyakrylat, innehåller polyakrylatjoner också karboxylgrupper, vilka nästan samtliga är deprotoniserade. De spektra som mättes här var i stort sätt lika de spektra som mättes på deprotoniserade karboxylgrupper på glycin. De smärra skillnader som dock fanns skulle kunna återspeglä att det är fråga om olika starka syror.

8.2 Studier av surfaktant/polyionkomplex

Vissa läkemedel kan klassificeras som surfaktanter och surfaktanttegenskaperna kan då i vissa fall användas i läkemedelsformuleringar (t.ex. tabletter eller kapslar). Exempelvis kan det utnyttjas för att skydda läkemedlet från nedbrytning på sin väg i mage och tarm eller genom att man kan styra friskättningen av läkemedlet, d.v.s. hur snabbt det portioneras ut från formuleringen till mag- och tarmafter och vidare ut i kroppen. Surfaktantmiceller kan bilda väldigt stabila komplex med polymerer, alltså långa kedjelika eller nättlika molekyler och sådana komplex skulle kunna användas som läkemedelsformuleringar. För formeringen av sådana komplex är en transportmekanism som diffusion viktig och där de monomera surfaktantmolekylernas rörlighet (mobilitet) är central.
I ett av avhandlingens arbeten bestämdes mobiliteten hos den monomera andelen av en surfaktant (dodecyltrimethylammoniumjon) i ett sådant komplex vid några temperaturer i intervallet 22 °C – 65 °C. Micellstrukturen visade sig bero på provets temperatur och strukturbestämningar gjordes vid några temperaturer i samma temperaturintervall. Strukturbestämningarna visade att micellerna är sfäriska vid 22 °C och avlångt cylindriska vid 65 °C medan båda formerna förekommer i temperaturintervallet däremellan och där andelen cylindriska miceller ökar med temperaturen. Mobilitetsbestämningarna visade att monomermobiliteten ökar med temperaturen och därmed också med andelen cylindriska miceller. Slutsatsen av detta är att micellerna troligen förmedlar transporten av monomerer och att de cylindriska micellerna, p.g.a. sin utsträckning, är effektivare än de sfäriska micellerna på detta.

Mobiliteten i dessa experiment mättes med hjälp av dielektricitetsspektroskop; också kallad impedansspektroskop. Detta är en elektrisk mätmetod, där man lägger på olika växelspänningar över provet och mäter de växelströmmar detta ger upphov till. En laddad partikel i provet, t.ex. en surfaktantjon, kommer på grund av växelspänningen att påverkas av en kraft som sätter jonen i rörelse vilket i sin tur ger upphov till en växelström. Ju högre jonens (molekylens) mobilitet är, desto mer lätt påverkad kommer jonen att vara av den pålagda växelspänningen. Mobiliteten kommer då att avspegla sig i växelströmsresponsen i hur stor den är och vid vilket frekvensintervall av pålagd växelspänning den uppträder. Responsens storlek kommer förutom mobiliteten också att vara beroende av antalet joner. Man kan alltså utifrån hur växelströmsresponsen ser ut, bestämma antalet monomera surfaktantjoner och dessas mobilitet.

Strukturbestämningarna i denna studie gjordes med hjälp av röntgendiffraktion (ej att förväxla med röntgenspektroskop ovan). Denna metod utnyttjar röntgenstrålningens vågsegenskaper. Man låter röntgenstrålning spridas mot olika delar av provet och mäter sedan intensiteten av den spridda strålningen i olika punkter en bit bort från provet. Det intensitetsmönster (interferensmönster) man får fram återspeglar de geometriska förhållandena i provet och man kan alltså ur interferensmönstret få fram, t.ex. den kristallform miceller formar eller den geometriska formen av miceller.

8.3 Modellering av frisättning av surfaktanter från ett binärt surfaktantsystem

Man kan också blanda två surfaktanter och i ett sådant tvåkomponentsystem (binärt system) kan man få miceller som innehåller båda typerna av surfaktanter. Tidigare studier har visat att man kan styra frisättningen från ett sådant system genom att ha olika proportioner av de två surfaktanterna. I ett av
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