Polymer Brushes on Flat Surfaces:

A Model System

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Abbreviations and Acronyms

CCA  α-cyano-4-hydroxycinnamic acid
DP   degree of polymerization
DSC  differential scanning calorimetry
PEO  poly(ethylene oxide)
PEG  poly(ethylene glycol)
TMS  tetramethylsilan
DMSO dimethylsulfoxide
NDP  N-dodecylpyridiniumchloride.
MALDI matrix assisted laser desorption ionization.
SCF  self consistent field
TGA  thermogravimetric analysis
ICP-AES inductively coupled plasma-atomic emission spectroscopy
VPO  vapor-phase osmometry
XRD  X-ray diffraction
Abstract

This work deals with the adsorption and properties of polymers at solid interfaces. The main purpose was to develop an experimental model system with well defined polymers and surfaces well suited for getting further insight into grafted polymers. Of special interest is the dependence on system parameters such as the degree of polymerization (DP), temperature, or solvent quality. Muscovite mica, a molecularly flat surface bearing exchangeable alkali cations at the accessible outer surface was used as the model surface. The polymers used were poly(ethylene glycol)s with several different DPs modified at one end with a cationic trimethylammonium group. The adsorption of the polymer was accompanied by an ion-exchange reaction of the polymer chain end, causing grafting. The specific surface area of the mica was increased chemically from 3-5 m²/g to ca. 100 m²/g. This was necessary in order to quantify the amount of polymer grafted to the surface thermogravimetrically. As determined from the crystal structure, muscovite mica contains ca. 4 µmol/m² exchangeable ions on the outer surface. With increasing chain length of the polymer grafted to the surface, less polymer molecules can be adsorbed, e.g., in aqueous solutions almost all inorganic surface ions can be exchanged with Methoxyethyltrimethylammonium bromide whereas only 10% of all surface ions can be exchanged with a cationic modified poly(ethylene glycol) of a DP = 47. The lower ion-exchange capacity of the polymers is a result of the steric hinderance of neighbouring chains on the surface. With increasing grafting density of head groups of the polymer on the surface, the polymers have to stretch perpendicular to the surface to form a polymer brush. This entropy penalty is compensated by an energy gain due to grafting of the head group. We applied molecular dynamics simulations to study the mica-water and mica-organic cation-water interface. From this simulations we obtained a good estimation that the cations used in our experiments are fixed into their cavities on the surface. The purpose of our experiments is to calculate the entropy penalty from experimental available data and compare them to existing theories. For comparison, we have looked at the step-function model developed by Alexander and deGennes, the molecular dynamics simulations of Murat and Grest, and the self-consistent field theory of Milner, Witten and Cates. As a result, the entropy penalty calculated from the simulations of Murat and Grest closely parallel the loss in entropy with increasing chain
Diese Arbeit untersucht das Adsorptionsverhalten von Polymeren an flachen, festen Oberflächen. Das Ziel ist es, ein experimentelles Modellsystem zu entwickeln, um einen tiefere Verständnis von Polymeren auf Oberflächen zu bekommen. In diesem Zusammenhang spricht man auch von "polymer brushes". Als Modelloberfläche dient Muskovit Glimmer, der eine molekular flache, kristalline Alumosilikat Oberfläche besitzt. Alkalikationen, die an der frei zugänglich Oberfläche die negative Ladung der Alumosilikat Oberfläche kompensieren, können somit durch andere Kationen ausgetauscht werden. Als Modell-Polymere dienen Polyethylenglykole unterschiedlicher Kettenlänge, die endständig kationisch durch eine Trimethylammoniumgruppe modifiziert worden sind. Die Adsorption der organischen Kationen wird somit von einer lonenaustauschreaktion begleitet. Um thermogravimetrisch die Zahl der Polymere auf der Oberfläche zu messen, wurde zuvor die spezifische Oberfläche des Glimmers von 3-5 m²/g auf 100 m²/g erhöht. Die Bindung der Polymeren an die Oberfläche erfolgt nur durch die Kopfgruppe. Von der Kristallstruktur der Glimmeroberfläche kann man die maximale Ionenaustauschkapazität in mol/m² berechnen. In unserem Fall beträgt dieser Wert 4 μmol/m². Resultierend aus den Experimenten ergibt sich, daß mit zunehmender Kettenlänge der Polymeren immer weniger Polymermoleküle pro Oberfläche über die Kopfgruppe an die Oberfläche gebunden werden. Dieses Ergebnis zeigt deutlich den Einfluß der sterischen Platzbeanspruchung der größeren Polymermoleküle mit zunehmender Kettenlänge, z.B. kann in wässriger Lösung mit dem Molekül Methoxyethyltrimethylammoniumbromid fast jedes Alkaliion auf der Muskovit Oberfläche ausgetauscht werden, wohinge gen mit dem polymeren Kation mit x = 47 nur ca. 10% der Oberflächenkationen ausgetauscht werden können. Mit zunehmender Belegungsdichte auf der Oberfläche weichen sich die Polymerketten aus und müssen sich aus diesem Grund senkrecht zur Oberfläche strecken. Diese Streckung bewirkt einen Entropieverlust, der durch einen Energiegewinn durch die Bindung der...
1. Introduction

1.1 Polymers in solution

One of the simplest polymers are polymers like poly(ethylene) or poly(ethylene glycol). It is basically a long chain of beads, where each bead is called the repeating unit or polymer segment. If all segments have the same chemical composition, the polymer is called a homopolymer (homos = equal). Most polymers are more or less flexible, and in solution they tend to coil up. There are many ways in which the chain can fold, and this leads to the high conformational entropy that is typical for polymers. The gigantic number of ways in which a flexible polymer in dilute solution can be arranged is a major problem in any attempt to model them. If there are only a few molecules in a large amount of solvent the coils will not overlap, not even when they are close together. Because two individual coils have more ways of arranging themselves internally than one big coil consisting of two chains, as the chains cannot intersect. One of the simplest models is the so-called random walk, in which a conformation of a polymer chain is approximated by a sequence of steps. The step length is fixed, but the direction in which the step is taken is completely random, and independent of all previous steps. This approach is analogous to the random-flight model used in describing the trajectory of a randomly diffusing particle (Brownian motion). As the average displacement of a particle in a given period of time is zero, it is customary to use the root-mean-square displacement (basically the standard deviation) as a characteristic parameter. In a similar way, the average size of a polymer coil is generally denoted by its radius of gyration, $R_g$.

For a random walk the radius of gyration turns out to be proportional to the square root of the number $N$ of steps taken, so that $R_g = N^{1/2}$. However, Flory has shown that in a good solvent, where the interaction between polymer segments and solvent molecules is favorable, the radius of gyration scales as $R_g \approx N^{3/5}$ with $N$ equivalent to the number of polymer segments. The difference is due to the so-called excluded volume effect: the random-walk model permits the backfolding of a chain onto itself, whereas in reality two segments cannot hold the same position at the same time. This causes the coils to swell.
Nevertheless, it turns out to be possible to find random walk statistics in a dilute polymer solution: if the interaction between polymer and solvent is sufficiently unfavorable, the polymers shrink. At a specific temperature, called the theta-temperature, the contraction of the coil due to the attractive interactions exactly cancels the expansion due to the excluded volume effect. Beyond the theta-temperature, where the solvent is very poor, the polymers are in a collapsed state, and $R_g = \sqrt[3]{N}$. Upon increasing the concentration of polymer, a concentration is reached where the total volume of coils equals the volume of the container. This is called the overlap concentration. If we take a sphere with radius $R_g$, then the overlap concentration $c^*$ can be found to scale as $N/R_g^3$. Beyond this concentration, the coils overlap. The solution then resembles a network with average mesh size $\xi$. This mesh size can be viewed as a correlation length: on length scales larger than $\xi$ a polymer segment cannot distinguish any longer to which polymer chain it is connected. The solution is semi-dilute. The overall shape of the network would not change if one of the polymer chains were cut in half, so that the chain length is not a characteristic length scale in a semi-dilute solution. Therefore, in a semi-dilute solution, the chain length can conveniently be left out of the description of the system. For a general overview see ref. [3-14].

In semi-dilute solutions, the correlation length does not depend on the chain length, but on the concentration: the more polymer, the more the network is squeezed. In other words, the correlation length in a semi-dilute solution $\xi_{sd}$ decreases with increasing the concentration. In order to find the concentration dependence on the correlation length, we can write the power law $^{[15]}$ as $\xi_{sd} = \xi_d (c/c^*)^{-3/4}$, where $\xi_d$ is the correlation length in a dilute solution, $c$ is the concentration and $c^*$ the overlap concentration. Next, we adjust the exponent $\alpha$ such that the outcome is independent on the chain length $N$, using Flory's radius of gyration. This leads to $\alpha = 3/4$, or $\xi_{sd} = c^{-3/4}$. If we increase the polymer concentration even further to the point where hardly any solvent is still present, we have a polymer melt. In a polymer melt all interactions are efficiently screened out, and the system behaves ideally, i.e., the polymers follow random-walk statistics.
1.2 Polymer adsorption

Long, flexible polymers in solution are colloids (or, in Staudinger’s terms, eucolloids)\(^{[16]}\). More general, solid particles in a fluid substance are called sols. If the solid particles consist of polymers that do not dissolve readily, the sol is called a latex, named after the milky fluid that comes out of a rubber tree (Hevea brasiliensis). The difference between the polymer molecules in the core of the latex particles and those fully dissolved is the freedom of movement: the latter change the conformation continuously whereas the latex molecules are in a glassy or even crystalline state. When a flexible, soluble polymer is added to a latex, there are two possibilities: adsorption or depletion. If the dissolved polymer has a more favorable energetic interaction with the particles than with the solvent, it may adjust its conformations and stick to the particle surface. This phenomenon is called adsorption. Adsorption limits the number of ways a polymer can arrange itself (and hence, its entropy) considerably, so the energetic interaction of the polymer with the surface (the adsorption energy) has to be large enough to compensate this entropy loss. The point where the adsorption energy is just large enough to yield adsorption is called the critical adsorption energy. For smaller adsorption energies, the polymer will stay away from the surface, leading to a zone where no polymer is present. This region is called the depletion zone, and the polymer is said to be depleted from the surface\(^{[5]}\). Both adsorption and depletion can have a dramatic effect on the stability of a sol or emulsion\(^{[18]}\): depending on circumstances it can either lead to stabilization (protecting the sol from creaming, settling, or phase separating), or to flocculation. The control of stability is vital in all applications where colloids are used: in cheese production or in water purification the system is meant to flocculate, whereas in milk any phase separation is undesirable. In paints it is sometimes convenient to bring the system to the verge of flocculation, as the half-formed flocks are easily broken when poured or stirred, but still sufficient to prevent settling of the pigment particles. From the above examples it can be seen that with polymer adsorption and depletion, polymer science has found its way back into colloid science: colloid scientists need polymers that comply with all the specifications needed, and polymer scientist know how such polymers should look.
Theories, approximations and their problems

A simple general strategy for the design of a polymer adsorption theory is to calculate all possible conformations of a polymer at the surface and in solution, count all interactions, derive the free energy of the system, and minimize it. For stability, also the effect of bringing particles together has to be taken into account. This procedure would yield all the information needed to predict the behavior of polymers near interfaces. Unfortunately, this method is in general unfeasible as the number of conformations is too large. Therefore, approximations and model assumptions have to be made. These theories use several approximations:

1. Markov chain: We have already encountered one popular approximation in the random-walk model. The basic assumption here is that the position of the segments are only influenced by the position of the segment immediately preceding them. This ensures the chain connectivity but it cannot prevent backfolding. A series of events where the current state only depends on the previous state is called a Markov chain.

2. Random mixing (Bragg-Williams) and mean field: This famous theory uses usually a lattice as in the Flory-Huggins (F-H) theory\[2\]. It was proven to be very successful in describing the thermodynamics of polymer solutions, predicting qualitatively the phase separation between different polymers and the possibility of fractioning polymers with the same chemical composition but different molecular weight. However, the precise behaviour of a polymer solution near the point of incipient phase separation is far from experimental findings. Mean-field theories (as the F-H theory) are infamous for their incorrect predictions of systems near a critical point. This discrepancy derives from the neglect of correlations. One could try to calculate the probability of inserting another polymer molecule in such a way that none of the segments of the molecule to be inserted will overlap with any segment of the polymers already present. Such a procedure could, e.g., be used in the calculation of the chemical potential of the polymer. If the total volume fraction of polymer segments is denoted as $\Phi$, the probability that any single segment can be inserted properly is $1 - \Phi$. But it is obvious immediately that there will be a pronounced
difference concerning the exact position of the first segment placed: the other segments stand a very good chance of hitting one of the segments already there. So, for all the other segments of the polymer to be inserted $1 - \Phi$, the average value for the excluded volume, is a very bad approximation for the probability that they will fit in. The method would be correct if the polymer segments were not connected but distributed in the solution at random. Therefore, this approximation is called the random mixing approximation. It is also known under the name Bragg-Williams approximation. The idea to tag one molecule and let the role of all other molecules be to form an average external field that acts on this tagged molecule is the basis of a mean-field approximation. The use of a Bragg-Williams approximation implies the use of a mean-field approximation, but not the converse: it is readily possible to improve on the Bragg-Williams approximation, e.g., by using a so-called quasi-chemical approach\(^{[17]}\), where correlations between nearest neighbours are taken into account, but still using a mean-field approximation.

3. **Interactions**: So far, we have mainly been concerned with entropic (excluded volume) interactions. As soon as we consider good or bad solvents, energetic aspects enter the discussion. Energetics are generally modelled by assuming a specific equation for the energy as a function of the interparticle distance and sometimes also by the orientation between particles (segments, molecules or even voids). Next, a cut-off has to be defined: it is impossible to calculate the influence of a particle upon the rest of the universe, but one can start with the energetic interaction of the particle with its immediate surroundings. In a lattice, this is especially convenient as the nearest neighbours and the distance between them are well-defined. In this case, it is enough to simply define a contact energy.

4. **Ground state dominance**: The random walk model for a polymer molecule is analogous to the random-flight model for a single Brownian particle. This analogy can also be used in polymer adsorption theories as a popular chain connectivity equation resembling a diffusion equation or even the Schrödinger equation used in quantum mechanics\(^{[19]}\). This method is called the diffusion equation approach. However, a major difference between a diffusing particle and a polymer molecule is the fact that a
polymer molecule has two chain ends whereas the diffusing particle does not have a specific end. A polymer segment located near one of the ends will in general behave differently from a middle segment, as the ends have more freedom of motion. In many diffusion equation theories, the importance of the chain ends is neglected. Basically, the polymers are taken to be infinitely long. A term often used in this respect is ground state dominance, jargon stolen from quantum mechanics.

5. **Scaling**: Instead of evaluating all possible conformations of a polymer molecule and then simplifying with approximations, it is also possible to coarsen the system by using “blobs” having a diameter equal to the correlation length\textsuperscript{[15]}. In this way, no details on a scale smaller than the correlation length can be obtained, but important physical laws can be derived without intricate mathematical methods.

6. **Equilibrium**: An important remark that has to be made here is that in deriving a minimum in free energy, one assumes that the system is in equilibrium. As stated before, polymers move very slowly in solution, so that in dense polymer systems it is very well possible that equilibrium is never obtained. For additional references on polymer brushes, see refs. 20-23.

1.3 **Mica and Other Layered Silicates**

The hydrous layer silicates commonly known as clay minerals are part of a larger family of phyllosilicates. The layer silicates contain continuous two-dimensional tetrahedral sheets of composition \( T_2O_5 \) (\( T = \) tetrahedral cation, normally \( Si^{4+}, Al^{3+}, \) or \( Fe^{3+} \)), in which individual tetrahedra are linked with neighboring tetrahedra by sharing three corners each (basal oxygens) to form an hexagonal mesh pattern. The fourth tetrahedral corner (the apical oxygen) points in a direction normal to the sheet and, at the same time, forms part of an immediately adjacent octahedral sheet, in which individual octahedra are linked laterally by sharing octahedral edges.
The common plane of junction between the tetrahedral and octahedral sheets consists of the shared apical oxygens plus unshared OH groups that lie at the center of each tetrahedral six-fold ring at the same z-level as the apical oxygens. Fluorine may substitute for OH in some species. The octahedral cations normally are Mg\(^{2+}\), Al\(^{3+}\), Fe\(^{2+}\), and Fe\(^{3+}\), but other medium-sized cations also occur in some species. The smallest structural unit contains three octahedra. If all three octahedra are occupied, i.e. have octahedral cations at their centers, the sheet is classified as trioctahedral. If only two octahedra are occupied and the third octahedron is vacant, the sheet is classified as dioctahedral.

The assemblage formed by linking one tetrahedral sheet with one octahedral sheet is known as a 1:1 layer. In order to accomplish this linkage, the upper tetrahedral sheet must be inverted so that its apical oxygens points down and can be shared with the octahedral sheet below. If the 1:1 or 2:1 layers are not electrostatically neutral, the excess layer charge is neutralized by various interlayer cations. The total assemblage of a layer plus interlayer is referred to as a structure unit.

Muscovite mica is a layered silicate mineral made up of ca. 10 Å thick silicate sheets bound together by potassium ions. The surfaces are molecularly flat, and, for that reason, mica sheets are extensively used as the substrate in AFM, STM, and surface force measurements studies.

The mica structure consists of negatively charged 2:1 layers that are bound together by large interlayer cations. In the true micas considered here interlayer cations are univalent, whereas in the brittle micas it is divalent. The layer charge in true mica ideally is -1.0 per formula unit and arises by some combination of three mechanisms:

1. substitution of R\(^{3+}\) (Al, Fe, Cr) for Si\(^{4+}\) in tetrahedral positions,
2. substitution of R\(^{1+}\) or R\(^{2+}\) for R\(^{2+}\) or R\(^{3+}\) in octahedral positions, or
3. substitution vacancies in octahedral positions.

The resultant layer charge may originate entirely within the tetrahedral sheet or entirely within the octahedral sheet in some species, or may come partly from both sheets. It is also possible for the octahedral sheet to have an excess positive charge, which is always
the case when the tetrahedral charge exceeds -1.0. A typical 2:1 layered structure can be seen in Figure 1.1.

Figure 1.1 Mica sheet with tetrahedral (T) and octahedral parts (O). Not drawn are the inorganic cations sandwiched by two TOT-layers.
References


2. The Structure of Ultra-High-Surface-Area Mica

2.1 Introduction

Layered silicates are widely modified with organic or inorganic cations. Many layered silicates, such as montmorillonite or vermiculite form interlayer complexes with a variety of neutral and positively charged organic compounds. In mica, however, interlayer complexes are not observed at ordinary conditions, though a slow intercalation may occur at 70°C. Also, while the inorganic interlayer cations in minerals such as vermiculite, montmorillonite or hectorite are hydrated, to an extent depending on humidity, the interlayer cations in micas are not hydrated (for refs. see [1-4]).

Most work on modification of layered silicates was performed with, e.g., montmorillonite, vermiculite, bentonite or hectorite, while relatively few studies deal with mica. This is probably due to the relatively low fraction of individual silicate layers available for the modification of the mica. For example, the ion exchange capacity of commercially available minerals is ca. 1 meq/g for montmorillonite and ca. 1-2 meq/g for vermiculite but only 0.001-0.02 meq/g for muscovite mica. As a consequence, the chemical analysis of the modified minerals with common methods often becomes difficult, due to the relatively low content of the modifying agent (e.g., organic cations) in the final product.

The ion exchange capacity of muscovite mica can be enhanced up to 1.2 meq/m² by treatment with lithium nitrate/water mixtures at 100-200°C[5]. It has been shown qualitatively, by measuring surface profiles of mica particles before and after lithium nitrate exposure, that the particles become thinner upon this procedure, i.e. a delamination takes place. The specific surface area determined with the BET method strongly depends on sample preparation: freeze-drying strongly enhances the surface area accessible to nitrogen molecules compared to filtration. This indicates that a large fraction of the individual particles are in close contact.
The delaminated mica was used for a number of surface modification studies, including organic and inorganic cations, polyelectrolytes, polymeric inclusion compounds and polymers with crown ether functionalities. A number of experiments showed that the delaminated mica contains lithium ions that can be substituted by other cations. The number of the exchangeable lithium ions depends on the reaction parameters. Typically a mica with an ion exchange capacity of ca. 0.4 meq/g was used, as measured by ion exchange with potassium, and N-dodecylpyridinium ions. Based on an ion coverage of 3.48 µmol/m², as determined from the crystal structure, the resulting specific surface area of the delaminated mica is ca. 100 m²/g, in agreement with surface area determinations with the methylene blue method. Methylene blue does not replace all the lithium ions of the delaminated mica (only ca. 0.25 eq/g), as also observed for other layered silicates.

In all the reports on the modification of the delaminated mica it was assumed that the modifying agents are present only at the surface, i.e., intercalation was not considered based on that intercalation is usually not observed in mica. In the present study, we present evidence for this assumption that the delaminated mica shows no intercalation but is a special cleaved mica with alternating lithium and potassium layers.

2.2 Treatment of micas with organic cations

Figure 2.1 shows X-ray diffraction patterns of delaminated and original (non-delaminated) mica. In the following, we refer to this mica as to mica A. The mica A structure is nothing else than the normal muscovite mica. The alumosilicate layered structure is sandwiched by potassium ions. No lithium ions are present in this structure. The original mica shows the characteristic 002 peak at a Bragg angle 2Θ of 8.8°, corresponding to a layer spacing of ca. 9.9 Å. After delamination with lithium nitrate new peaks can be observed at 2Θ values of 4.02° and 8.10° (Figure 2.1), corresponding to layer spacings of 21.5 Å and 10.9 Å. Additional peaks in these powder patterns refer to higher orders of the peaks mentioned above.
Figure 2.1 XRD-pattern of mica A and mica B. The mica B shows, in addition to the original peaks from the mica A structure, several additional reflections, indicating a larger d-spacing of the interlayer distances.

The new signals (in the grey region of Figure 2.1) indicate structural changes for the delaminated mica. In the following we refer to this mica structure as to mica B. The mica B is nothing else than a lithium nitrate treated mica A. This can be illustrated with the following reaction:

\[
mica A \rightarrow_{\text{LiNO}_3} mica B
\]

There can be seen further additional reflections indicating higher orders of the previous reflections. However, the reflections of the original mica (\textit{mica A}) are still present. These indications suggest that the delaminated mica contains (i) a significant fraction of mica in its original bulk structure, and (ii) a fraction of a mica with a new structure having a particle thickness below that of the original mica (broader signals). Also, the new peaks are broader than the original peaks indicating that the number of mica sheets per particle is lowered.
Both mica, original and delaminated, were treated with aqueous solutions of alkylammonium salts of the formula \((\text{CH}_3)_3\text{N}^+(\text{CH}_2)_n\text{CH}_3\), \(n=4, 6, 8, 10, 12, 14, 16, \text{ and } 18\) at 65 °C (see Chapter 7). These compounds are known to intercalate in clays.\(^9\) The X-ray diffraction patterns of the original mica do not change upon treatment with the alkylammonium compounds, i.e., there is no evidence for intercalation. Treatment of delaminated mica with the alkylammonium salts results in a shift of the reflections of the two additional peaks at 2\(\Theta\) values below 10°, as can be seen in Figure 2.2.

![Figure 2.2](image)

**Figure 2.2** Reaction of mica B with alkylammonium salts of different chain length. The 001 reflection for the uncleaved mica A is indicated with the dashed arrow. The dashed lines indicate the shift of the first and second new peaks with respect to the chain length and are just guides to the eyes.

The positions of the peaks decreases with increasing chain length of the alkylammonium compounds. The ratio of the layer spacings for the 001 (peak at lower 2\(\Theta\) values) and 002 (peak at higher 2\(\Theta\) values) reflections are given in Table 2.1. The constant ratio of ca. 2 shows a correlation of these two peaks (001 and 002).
Table 2.1
Ratio of the 001 and 002 peak for different intercalation agents.

<table>
<thead>
<tr>
<th>length of the alkyl chain</th>
<th>layer distance d (Å)</th>
<th>ratio: 001/002</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>first</td>
<td>second</td>
</tr>
<tr>
<td>C4</td>
<td>24.68</td>
<td>12.35</td>
</tr>
<tr>
<td>C6</td>
<td>27.02</td>
<td>13.61</td>
</tr>
<tr>
<td>C8</td>
<td>29.35</td>
<td>14.68</td>
</tr>
<tr>
<td>C10</td>
<td>31.16</td>
<td>15.77</td>
</tr>
<tr>
<td>C12</td>
<td>32.66</td>
<td>16.52</td>
</tr>
<tr>
<td>C18</td>
<td>44.17</td>
<td>21.45</td>
</tr>
</tbody>
</table>

The intensity of the first peak increases with increasing chain length while the second peak decreases; this is due to the layer scattering amplitude $F_{hkl}$.

A similar behavior is also observed after treatment of other clay minerals bearing a lower surface charge density $\sigma$ with alkylammonium ions. These results are explained in terms of an increased space requirement of the intercalated alkylammonium chains.

2.3 Modelling of X-ray diffraction pattern

2.3.1 Analytical methods

In order to explain the results described above (see Chapter 2.2), the 001 reflections of various X-ray diffraction patterns are simulated. Some simulation methods have been developed in the last few years to calculate powder diffraction patterns for clay minerals\textsuperscript{10}. Nevertheless, a simplified model system would explain the structural changes in detail. The following models were considered: intercalation in alternating layers and intercalation in each layer of a mica particle (Figure 2.3).
Figure 2.3. Schematic figures of the two considered models. (i) represents the alternating-intercalation model, where we assume an exchange of inorganic ions against alkylammonium salts in every second layer. (ii) assumes an exchange with alkylammonium ions in every layer.

The equations for X-ray diffraction of powder samples were developed by Debye\[11\]. For composite assemblies of N scatterers\[12\], the following two equations (eq. 2.1 and eq. 2.2) are most general

\[
I(q) = \sum_{i=1}^{N} I_i(q) + 2\sum_{i}^{N} \sum_{j>i}^{N} f_i(q)f_j(q) \frac{\sin(qr_{ij})}{qr_{ij}}
\]  

(2.1)

where
Eq. 2.1 shows the dependency of the intensity $I(q)$ on the atomic structure factors $f$ and on the position of the scatterers. The length of the scattering vector $q$ is given by eq. 2.2, where $\lambda$ denotes the wavelength and $\Theta$ refers to the Bragg angle. These two equations are only valid for infinite crystal size. For the structural analysis we are interested in peak positions rather than in intensities for analysis of the powder pattern. Therefore, we consider $I_i$ and $f_i$ independent of $q$. Furthermore, we take $f_i \sim f_j$ as equal and the terms in the double sum much larger than $N$. The intensity $I(q)$ is generally given by

$$I(q) = \iiint \rho^2(r) \exp(-iqr) \, dV \approx \int P(z) \exp(-i\mathbf{q} \cdot \mathbf{z}) \, dz \quad (2.3)$$

In eq. 2.3, we have introduced a factor $P(z)$ representing the autocorrelation function $\rho(r)$ for a given plane 00l in the $z$-direction. The axial ratio of particles is very large, i.e. $>100$, and therefore the $hkl$-reflections are independent of the particle thickness. As a result, only the 00l-reflections will be discussed. The calculation of powder patterns is simplified by calculating the autocorrelation function $P(z)$ which depends on the size of the particles. The size of the particles in the $z$-direction can be described by a binomial distribution of the mica particles in the $z$-direction. The aspect ratio of the delaminated mica particles is more than 100.

The number of layers in a particle is represented by a distribution function $w(n)$, and the mean thickness $<D>$ becomes $<D> = <n>d$. The factor $P(z)$ can be evaluated for model systems according to the frequency of the layer spacing $d$. For a common mica structure without intercalation, the $P(z)$ factor can be written as

$$P_R(nd) = \sum_{i=n}^{n_{\text{max}}} (i-n+1) w(i) = P(z), \quad (2.4)$$

where $n_{\text{max}}$ denotes the maximum number of layers possible, $w(i)$ is the probability of an $i$-layer distance and $n$ is the index for the reflection.
Figure 2.4 The three models in another light. The \( \Delta \) spacing mimics an intercalation with a thickness of \( \Delta \).

The probabilities of the intercalation models are developed according to Figure 2.4. The following table lists all the probability relations that are necessary to simulate the three different models. (Table 2.2).

**Table 2.2**

<table>
<thead>
<tr>
<th>reflection</th>
<th>alternating-intercalation</th>
<th>total-intercalation</th>
<th>mica A</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P(nd+[n-1]\Delta) )</td>
<td>-</td>
<td>( P_R(r) )</td>
<td>-</td>
</tr>
<tr>
<td>( P(nd+n\Delta) )</td>
<td>-</td>
<td>2( P_R(r) )</td>
<td>-</td>
</tr>
<tr>
<td>( P(nd+[n-1]\Delta) )</td>
<td>-</td>
<td>( P_R(r) )</td>
<td>-</td>
</tr>
<tr>
<td>( P(nd) )</td>
<td>( \sum_{i=1}^{n_{max}} i w(i) )</td>
<td>-</td>
<td>( P_R(r) )</td>
</tr>
<tr>
<td>( P(d+\Delta) )</td>
<td>( \sum_{i=1}^{n_{max}} i w(i) )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( P(2d) )</td>
<td>( \sum_{i=1}^{n_{max}} \frac{i}{2} w(i) )</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2.2
Probability relations

<table>
<thead>
<tr>
<th>reflection</th>
<th>alternating-intercalation</th>
<th>total-intercalation</th>
<th>mica A</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(nd+n/2Δ)</td>
<td>$\sum_{i=n}^{n_{mix}} \left[ 2 + 3 \frac{(i - n)}{2} \right] w(i)$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The calculation of $P(z)$ results, after discrete Fourier transformation (DFT), in a powder pattern for each of the models. The analytical method is shown here only for completeness of the possible ways by which powder pattern can be derived for layered structures, where only two different spacings exist. With the analytical method, it is not possible to discuss random distributions of two interlayer spacing length $d$ and $\Delta$. Therefore, the numerical solution for $P(z)$ is a much more elegant way to analyze the powder patterns.

![Example of a simulation of the powder patterns for the mica A structure.](image)
2.3.2 Numerical Methods

For the generation of $P(z)$, we performed a step-by-step addition of unit cells, where the type of unit cell is chosen with a certain Bernoullian probability (Figure 2.6).

![Diagram showing the particle generation procedure.](image)

**Figure 2.6** The particle generation procedure. The addition of the next layer-type $x$ or $y$ can either be an interlayer spacing $d$ or $\Delta$, or a complete unit cell that is added to an already existing sequence of layers. In this context, the probability $p$ denotes the probability of adding $X$ instead of $Y$. The probability $q$ denotes the probability of the sequence of $X$s and $Y$s.

Generating a mixture of unit cells, i.e. those for the “alternating-intercalation”- and “total-intercalation” type, is straightforward. In the following, we consider particles consisting of one intercalation type and non-random mixing. Inserting these probabilities $P(z)$ in eq. 2.4 gives, after discrete Fourier transformation (DFT), the desired powder pattern. The calculated powder patterns are shown in Figure 2.7 for different model systems with fixed $d$ - spacing of 10 Å and fixed $\Delta$ - spacing of 4 Å. The values are chosen according to a layered structure, where the size of the layers is equivalent to $d$. 

\[ n \text{ layers with probability } q(n) \]
\[ \text{i.e. XXXYYYX } \quad (n = 6, q = p^4(1-p)^2) \]

Choose the next layer-type ($X$ or $Y$) with a probability $p$.

\[ r < p \quad \text{Add layer-type } X \]
\[ P(n+1) = pqw(N) \]
\[ (n = 7, q = p^5(1-p)^3) \]

\[ XXXYYYX \]

\[ r \geq p \quad \text{Add layer-type } Y \]
\[ P(n+1) = q(1-p)w(N) \]
\[ (n = 7, q = p^4(1-p)^3) \]

\[ XXXYYXY \]

\[ \Rightarrow \text{XXXYYYYXXYX} \quad \text{stacking sequence of xy-layers} \]
and the intercalation is equivalent to $A$. The powder patterns, in Figure 2.7, show the Fourier transformed results for the probability function $P(z)$. The powder patterns, as derived by the analytical method, are equal to the ones derived numerically for the three models.

The data are convoluted with the Lorentz-polarization (eq. 2.5) function for powder patterns to correct for the polarization effects of the X-ray beam.

\[
\frac{1 + \left[ \cos (2\Theta) \right]^2}{\sin \Theta \sin 2\Theta}
\]

(2.5)

Therefore, it is not possible to derive absolute intensities (see Introduction of this Chapter). However, if we are interested in relative intensities and peak width, the new model gives accurate results. Before further elaborating on this model, it is desirable to compare our technique with methods already used for the calculation of powder patterns in order to prove the correctness of the calculated peaks.

2.3.3 Calculating the X-ray powder patterns from the atomistic structure

It is also possible to calculate the X-ray powder patterns for layered silicate structures with commercially available software. We have used the INSIGHT program from MSI (San Diego) for the calculation of diffraction patterns of the mica structures using the complete atomistic structure and structure factors. The intensity is calculated according to eq. 2.6.

\[
I(q) = \sum_j \sum_k f_j(q) f_k(q) \exp (i r_{jk} q)
\]

(2.6)

Simulation of the scattering parameters, from a given structure, requires knowledge of the projections of each of the interatomic vectors, $r_{jk}$, on the scattering vector, $q$. To adjust different observations to the same absolute scale requires the application of correction factors that depend on the scattering angle and the geometry of the measurement. This can be done by using the Lorentz-polarization factor that takes such problems into account. This factor is determined by the measurement geometry and is independent of the type of radiation used. The polarization factor only applies to X-ray diffraction. Due to the polarization of an unpolarized incident beam, when diffracted
Figure 2.7 Calculated powder patterns for the three model systems (see text). The convolution of the raw data was done by using the Lorentz-polarization factor (next page).
from the crystal, we have to correct the simulations because of a reduction of the scattered intensities.

For powder diffraction, the polarization correction for X-rays is similar to that for single crystals, although the Lorentz factor is different in form. We have used the combined Lorentz-and polarization factors for the Debye-Scherrer method. Also, we correct the results for preferred orientation according to Dollase.\textsuperscript{[13]}

The structure of dioctahedral mica was derived from the literature\textsuperscript{[14]}. This refined mica structure best represents the delaminated mica structure. The unit cell was build up and the powder patterns were calculated using the MSI-Software package INSIGHT. The powder patterns were derived for the different models with different intercalations and were also plotted for the pure mica structure (Figure 2.8).

\textbf{Figure 2.8} Calculated powder pattern for three different stacking sequences. The top-most diffraction pattern reflects for the untreated muscovite mica structure. The diffraction pattern, in the middle, (b) reflects the powder pattern of a mica with an intercalation of 4 Å in every second layer. The last pattern (c) shows the diffraction pattern of a muscovite mica with a 4 Å intercalation in every layer.
Also calculated are the hkl-reflections not occurring in the measured powder pattern due to the texture of the sample for the X-ray diffraction. These samples behave like a stack of paper sheets lying on each other. This leads to a more or less oriented distribution of the powder because the orientation of the sample. The 00l planes of the mica orients parallel to the glass slide, on which the mica was deposited on for the X-ray diffraction measurements. This orientation is much more probable than an orientation perpendicular to it. Therefore, the measured intensities for the reflections other than the 001 are largely reduced. Further, the computer simulations assume a random distribution of the crystallites and, give much higher intensities, also for peaks not visible in the experimental powder pattern.

2.4 Results and Discussion

Sharp peaks, corresponding to the signals of untreated muscovite mica, and broad peaks can be observed in the experimental patterns of the lithium nitrate treated mica. In particular, the sharp peak at a 2\( \Theta \) value of 8.8° corresponding to a 10 Å layer distance appear in any pattern. It is likely that the samples of lithium nitrate treated mica (mica B) consist of a mixture of particles of “mica A” and of modified particles. In order to elucidate the structure of the modified particles, the above mentioned models are used to compare hypothetical structures with the experimental data.

If the patterns of the untreated mica and the lithium treated mica are mixed, the experimentally observed powder pattern can be derived (Figure 2.9).

For the simulation of the broad signals, the following models are considered: substitution of potassium ions in every layer and substitution in every second layer. The pattern obtained with our new method yields the same pattern as those obtained from the atomistic simulation. From the atomistic simulation, we obtain the same result as for the experimental pattern of our delaminated material, and we must therefore assume a mixture of layered silicates in the delaminated mica. The comparison of simulated X-ray diffraction patterns and the experimental pattern of delaminated mica leads to the conclusion that the broad signals, at reflections with 2\( \Theta \) smaller than 8.8°, belong to a
mica in which every second layer contains lithium ions, and that the small broad signals at 7.4° are due to reflections of mica particles where each interlayer is exchanged by lithium ions. Figure 2.10 shows spectra calculated for a mixture of original mica and the two types of mica with modified interlayers.

**Figure 2.9** Theoretical fit (lower curve) and experimental powder pattern (top curve) for the pure mica structure.

**Figure 2.10** Calculated and experimental powder patterns for the delaminated mica. The top one represents the experimental pattern. The lower one represents the sum of the three individual powder patterns calculated.
Analogously, the experimental X-ray spectra of the alkylammonium-treated mica can be composed from the individual spectra of original mica, in which every second layer contains alkylammonium ions and a small fraction of mica in which alkylammonium ions are present in every interlayer (Figure 2.11).

![Figure 2.11](image)

**Figure 2.11** Theoretical and experimental powder patterns of treatments with C6- (top) and ClO−-alkylammonium salts (bottom). The peak pattern of the experimental powder patterns (the topmost curve in every plot) is fitted using the "total"-intercalation, the "alternating"-intercalation model, and the mica A - model. The theoretical calculations are plotted below the corresponding experimental patterns (thin line).

Considering the Bragg equation

\[ \Delta(2\Theta) = \frac{0.9\lambda}{B\sin(\Theta_0)} \]  

(2.7)

that relates the peak width \( \Delta(2\Theta) \) at half intensity of the peak to the stacking number of
silicate layers lying on each other, the average number of silicate layers in a particle can be calculated\(^ {\text{[15]}\)\). The thickness of the particles of the original mica (110 layers) decreases to ca. 50 layers upon the lithium nitrate treatment, as can be determined from the broadening of the diffraction pattern. The particles with modified interlayers are thinner than the particles with the original mica structure. It seems, therefore, that the original mica is not delaminated by a stochastic interlayer modification, but that first interlayer modification with lithium induces further interlayer modifications.

2.5 Conclusions

As determined experimentally, the ion-exchange capacity of mica A is increased by chemical treatment with lithium nitrate. In this chapter, we have looked at the reasons of this increased ion exchange capacity. It can be shown, by X-ray diffraction analysis and treatment of mica B with several alkylammonium salts of different chain length, that the increased ion exchange capacity is due to an exchange of potassium ions against lithium ions during chemical treatment with lithium nitrate. Normal mica A is not swellable in aqueous solutions. This is due to potassium ions fitting best into the surface cavities of the alumsilicate tetrahedra. The replacement of potassium ions against lithium ions leaves some space also for water molecules such that these layers can be swollen\(^ {\text{[8]}\)\). Therefore, mica B swells in water, the sheets delaminate and the ion exchange capacity will be increased.
References


3. Polymeric Surface Modifications via Ion Exchange

3.1 Introduction

A number of theoretical and experimental studies have dealt with polymer chains terminally attached to inorganic surfaces (for reviews, see refs. [1,2]). While in some cases the macromolecules are surmised to be attached to the surface via covalent bonds, in other studies the chains are, or are assumed to be reversibly adsorbed and in equilibrium with the contacting solutions. Cases in which there is unambiguous experimental evidence for the nature of the polymer-surface interactions are relatively rare: Poly(ethylene oxide) (PEO) with amino or triethoxysilyl end groups can be grafted to silica or surface-modified silica[3][4] and there are also a number of investigations of aqueous PEO solutions in contact with inorganic surfaces[5]. To our knowledge, none has dealt with ion-terminated chains, and few experiments have been reported in which the influence of the molecular weight on the number of adsorbed chains was measured[1][2].

On surfaces of layered silicates such as mica, polyelectrolytes can be attached by ion exchange[6-8]. Mica with its molecularly flat surface is a particularly attractive substrate for surface studies and it is indeed widely used in atomic force microscopy, scanning tunneling microscopy, and surface force measurement studies[9-11] and offers the possibility of studying the ion exchange equilibrium adsorption of cation-end-group polymers on an inorganic substrate with well defined end-group-to-surface interactions. Here, we examine the modification of mica surfaces with PEO chains having cationic endgroups. The cationic PEO- mica system is, we believe, a convenient and sensitive model system, with a set of parameters that can be varied to test and extend existing theories about end-tethered polymers at surfaces.
3.2 Experimental

In Figure 3.1, the synthesis of the cationic modified poly(ethylene glycol) is described. For all the cationic polymers, we have applied the same synthetic method to turn the hydroxy group into the ammonium group. Poly(ethylene glycol) is good soluble in toluene. The synthesis of (2) can easily be achieved with thionylbromide in toluene under reflux. The bromine endgroup by itself serves as a good leaving group to form the quaternary ammonium ion (3).

For detailed description of the synthesis see Chapter 7.

\[
\begin{align*}
\text{SOBr}_2 / \text{toluene} & \quad \text{reflux} \\
\text{N(CH}_3)_3 / \text{ethanol} & \quad 373 \text{ K, 2 bar}
\end{align*}
\]

\[
(1) \quad \rightarrow \quad (2) \\
\quad \rightarrow \quad (3)
\]

Figure 3.1 Synthesis of the quaternary trimethylammonium compounds. The compound (1) refers to the starting material.

According to Bückmann et al.\textsuperscript{[12]}, the quaternary trimethylammonium terminated poly(ethylene glycol) (3) can be obtained. In order to verify that the synthetic procedure has not changed the dispersity of our samples and in order to verify and quantify the molecular weights as well as the chain length exactly, the matrix assisted laser desorption ionization (MALDI-TOF) techniques have been used. In addition, the molecular weight was determined by vapor phase osmometry and end group analysis for
these samples. The MALDI technique has a much higher accuracy with respect to the NMR and vapor phase osmometry techniques in that molecular weight range. A representative example of the MALDI analysis can be seen in Figure 3.2.

3.3 Results and Discussion

The Polymers

Cationically terminated PEG's of two chain lengths and a low molecular weight compound (2-methoxyethyl-trimethylammoniumbromide) were prepared. The cationic polymers were analyzed with $^1$H-NMR spectroscopy, MALDI-TOF MS, vapor-phase osmometry, DSC, and TGA. Molecular weights and degrees of polymerization are displayed in Table 3.1. The values of $M_n$ obtained from MALDI-TOF MS, vapor phase osmometry, and NMR (by integration of the methoxy and the trimethylammonium end-group signal and comparison to the ethylene signal) are in excellent agreement. Two representative MALDI spectra (starting material and end-group-modified polymer for the case degree of polymerization (DP) $x = 47$) are shown in Figure 3.2.

Evidently, the molecular-weight distribution is very narrow, $M_w/M_n = 1.01$ (see also Table 3.1); in the following, we treat the polymers as pure compounds, i.e., uniform with respect to molecular weight, with DP of $x = 1$, $x = 47$, $x = 117$, and $x = 234$. 
Figure 3.2 MALDI spectra of, above, the hydroxy-terminated polymer with $x = 47$ and, below, cation-terminated polymer derived from it.
Table 3.1
Molecular characterization of the cation-terminated poly(ethylene oxide) chains employed in ion exchange on mica. Molecular weights are given without the bromine anion.

<table>
<thead>
<tr>
<th></th>
<th>‘x = 1’</th>
<th>‘x = 47’</th>
<th>‘x = 117’</th>
<th>‘x = 234’</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPO, $M_n$</td>
<td>-</td>
<td>2010</td>
<td>5550</td>
<td>10862</td>
</tr>
<tr>
<td>MALDI-TOF MS, $M_n$</td>
<td>-</td>
<td>2157</td>
<td>5238</td>
<td>10476</td>
</tr>
<tr>
<td>MALDI-TOF MS, $M_w$</td>
<td>-</td>
<td>2179</td>
<td>5290</td>
<td>10564</td>
</tr>
<tr>
<td>$^1$H-NMR, -CH$_2$-CH$_2$-O groups per CH$_3$-O-group</td>
<td>-</td>
<td>1.0</td>
<td>44</td>
<td>112</td>
</tr>
<tr>
<td>$^1$H-NMR, -CH$_2$-CH$_2$-O groups per (CH$_3$)N-group</td>
<td>-</td>
<td>1.0</td>
<td>43</td>
<td>105</td>
</tr>
</tbody>
</table>

VPO: vapor-phase osmometry in water at 50 °C;
MALDI-TOF MS: matrix-assisted laser desorption ionization time-of-flight mass spectrometry (matrix described in the text);
$^1$H-NMR: 300 MHz proton spectroscopy in d$_6$-DMSO at ambient temperature.

**Adsorption**

Some adsorption experiments were carried out in a conductivity cell. Because the mica, used here, has exchangeable lithium ions with considerably higher specific conductivity in aqueous solution than that of the organic ions. Upon ion exchange, the lithium ions on the mica surface will pass into the solution, replacing the newly adsorbed organic ions. The conductivity of the supernatant solution should increase, and, after mixing the polymer solutions and mica suspensions, the conductivity did indeed increase. As an example, the variation of conductivity with time for the cationic case of $x = 47$ is displayed in Figure 3.3.
It is clear that the exchange is essentially complete within a few minutes. Also, adsorption is fully reversible.

Adsorption experiments with the starting PEO polymers, i.e., chains bearing hydroxyl end groups instead of cationic end groups, reveal that no detectable adsorption occurs with these polymers. The cationic end group is, therefore, responsible for the strong attachment of the cation-terminated PEO chains to mica.

For each of the cationically terminated chains, adsorption experiments were carried out at different cation/mica ratios. The number of adsorbed organic cations was calculated from the mass of organic material determined by TGA. The resulting isotherms are
displayed in Figure 3.4 with the surface concentration of adsorbed organic cations, $\Gamma_a$, plotted against the total amount of organic cations added to the system relative to the total surface, $a$ (both in units of $\mu$mol/m$^2$ of mica surface as measured with methylene blue adsorption). The isotherm for $x = 1$ is similar to those previously reported for small ions on mica.

**Figure 3.4** Ion exchange isotherms of cation-terminated polymer with $x = 117$ (triangles), $x = 47$ (circles), and $x = 1$ (squares), as measured by TGA. The straight line has a slope of unity and corresponds to the limit of quantitative adsorption. The dashed line corresponds to the value of maximum exchange capacity. The curves are simply guides for the eye. The data for $x=234$ parallel the behaviour of the others with a lowered plateau value.
At low $a$, the adsorption is quantitative ($\Gamma_a = a$) and there is a "plateau" at high $a$ values where $\Gamma_a$ becomes substantially constant. For $x=1$, the plateau occurs at about 1.4 µmol/m$^2$ while for the polymeric ions $\Gamma_a$ is much smaller in the plateau regions, decreasing with increasing chain length. For $x = 47$, the plateau is at ca. 0.4 µmol/m$^2$, and for $x = 117$ ca. 0.2 µmol/m$^2$. That the polymers show such distinct plateaus is striking and perhaps surprising; it is as if the polymer chains each occupied a specific surface area, possibly determined by the size of the coil. However, since the polymer coils are interpenetrating at least to some degree, these plateaus are presumably only visual constructs. Nevertheless, the ion exchange capacity does appear to depend very clearly on the length of the chain attached to the ion, with decreasing capacity accompanying increasing length.

The release of lithium ions upon adsorption of the polymeric cations is shown in Figure 3.5. Evidently, the release closely parallels the adsorption (cf. Figure 3.4), demonstrating that ion exchange is indeed the adsorption mechanism. The differences between the curves for adsorption and release probably reflect the precision of the analytical methods or the presence of small amounts of adventitious cations that exchange to yield additional lithium ions. The fact that, within the experimental precision, one lithium ion is released per adsorbed organic cation shows that ion exchange accompanies the adsorption process tethering the chains to the surface. However, the adsorption process is controlled by free energy changes involving both enthalpic and entropic contributions.

The plateau values where the adsorption isotherms level off are shown in Table 3.2.

<table>
<thead>
<tr>
<th>x</th>
<th>1</th>
<th>47</th>
<th>117</th>
<th>234</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation coverage</td>
<td>3.4</td>
<td>0.45</td>
<td>0.25</td>
<td>0.11</td>
</tr>
</tbody>
</table>

These values are determined according to the method described in Chapter 5.
Figure 3.5 Release of lithium ions accompanying the adsorption of cation-terminated polymer with $x = 117$ (triangles), $x = 47$ (circles), and $x = 1$ (squares), as measured by ICP. The curves are simply guides for the eye. The dashed line corresponds, as in Figure 3.4, to the maximum exchange capacity, whereas the straight line corresponds to quantitative adsorption.

Several theoretical descriptions of polymer adsorption have been published. The Self Consistent Field (SCF) theory of Milner, Witten and Cates\textsuperscript{[15]}, further elaborated by Ligoure and Leibler\textsuperscript{[16]}, yields, in the limit of high surface coverage (i.e., stretched
chains), an exponential dependence of the surface coverage $\Gamma_a$ on the degree of polymerization $x$ of the chains$^{[16]}$:

$$\ln \Gamma_a \propto -x + c$$  \hspace{1cm} (3.1)

where $c$ is a positive term that depends on the concentrations in solution, the characteristic ratio of the chain, the excluded volume parameter, and the degree of crowding on the surface. At first blush, our data seems not to contradict this trend. A quantitative assessment follows in Chapter 5.

It is also interesting to note that the mean distance between attached chains and the plateau concentrations, estimated simply as $\Delta = \left(\Gamma_a N_L\right)^{1/2}$ (where $N_L$ is Avogadro's number), is of the same order as the radius of gyration of the unperturbed, free chain, computed as:

$$s = 6^{-1/2} l \left(C_\infty n\right)^{1/2}$$ \hspace{1cm} (3.2)

with $l = 0.15$ nm, $C_\infty = 4$, and $n = 3x + 1$ is the number of skeletal bonds in the chain: for $x = 1$, $\Delta = 0.7$ nm, $s = 0.2$ nm; for $x = 47$, $\Delta = 2.0$ nm, $s = 1.4$ nm; and for $x = 117$, $\Delta = 2.9$ nm, $s = 2.2$ nm. The fact that $s/\Delta$ is approximately the same for the polymeric compounds ($\approx 0.7$) might hint at a limitation of the surface coverage by interference between neighboring coils at the surface. It should be noted that for $a$ larger than the values shown in Figure 3.4, $\Gamma_a$ eventually passes through a maximum and begins to decrease. We speculate that the cause may be a change in the solvent quality at high $a$.

While the number of adsorbed ions decreased strongly with increasing molecular weight in the plateau region, the mass adsorbed actually increased, from ca. 2.7% w/w of the solid (mica plus organic cation) for $x = 1$, to ca. 8% w/w for $x = 47$ and ca. 9% w/w for $x = 117$. Thus, in the dry state, the thickness of the adsorbed polymer layer, assuming roughly constant density, increased. Presumably, then, this thickness can be influenced by the selection of the molecular weight, which may have some technological
3.4 Conclusions

Cation-terminated PEO adsorbs on mica surfaces via ion exchange to give a film of terminally attached polymer. The experimental ion-exchange isotherms resemble the isotherms for small cations, but with a reduced surface exchange capacity for the polymeric cations where the plateau value decreases with increasing degree of polymerization $x$. For the cations studied, the adsorbed mass increased with increasing chain length even though the number of adsorbed chains in the plateau region decreased. This allows modification of the (dry) thickness of the organic layer by selection of the molecular weight of the polymer. The ion-exchange process may be used to modify mineral surfaces.

We believe that ion exchange on mica also offers a sensitive new experimental method for studying the behaviour of chains tethered to a surface. The equilibrium between tethered chains and chains in the bulk solution can be readily measured and, due to the strong dependence of equilibrium constants on Gibbs-energy differences, this is a sensitive technique for studying chain behaviour. By changing parameters such as the degree of polymerization, the temperature, or the solvent quality, it should be possible to test and further develop theories for polymers and polymer brushes.
References


4. Molecular Dynamics Study of the Water-Mica Interface

4.1 Introduction

The orientational distribution of solvent molecules near an interface differs from that of the same molecules in solution. The orientation bias results from nonbonded interactions with the surface inducing a layering and structuring of near-surface solvent molecules and is largely responsible for interfacial phenomena such as wetting, swelling, and adhesion. A large number of experimental (for a sample see refs. [1-5]) and theoretical (e.g., refs. [6-9]) contributions towards this area of research have appeared (an excellent review can be found in ref. [10]). Here, we attempt to estimate the influence of a particular surface, muscovite mica, on the local structure and cohesive energies of solvent (water) and organic molecules grafted to the surface. Muscovite mica is a well characterized, atomistically flat aluminosilicate layered structure consisting of a negatively charged aluminosilicate TOT-layer (consisting in turn of a tetrahedral, and octahedral, and a further tetrahedral layer) and positively charged ions intercalated and at the surface. Structural aspects of this layered aluminosilicate mineral will be discussed in the next section. As counterions, we investigated the alkali cations and a quaternary ammonium salt because of its relevance to an experimental effort reported separately [11]. In particular, we have estimated orientation correlations for these small organic compounds at different surface coverages. As solvent, we consider water.

In Chapter 4.2, a presentation of the atomistic model and forcefield parameters are given as well as the descriptions of the systems under investigation with simulation details. Finally, in Chapter 4.3, the results from our atomistic simulation are summarized and discussed.
4.2 Atomistic Modelling

4.2.1 Mica Structure

Mica particles, as well as other layered clay minerals, consist of stacks of mineral sheets. Such a mineral sheet contains in the case of mica an octahedral layer of aluminium oxide, magnesium oxides, or other octahedral coordinated oxides, in between two tetrahedral layers of silica where one of the four silicon atoms is replaced by one aluminium atom. The arrangement of tetrahedral and octahedral oxide layers is called a tetrahedral-octahedral-tetrahedral (TOT) layer. The substitution of aluminium for silicon causes a negative charge in the tetrahedral layers, which is neutralized by positive interlayer cations, e.g., potassium. The ideal stoichiometric formula for muscovite mica is K[Al$_3$(AlSi$_3$)O$_{10}$(OH)$_2$. The atomistic mica structure employed here closely parallels the ideal muscovite mica $^2$M$_1$ structure and was obtained from the Cambridge Crystallographic Database$^{[12]}$. For the atomistic simulations, we address only one muscovite aluminosilicate TOT-layer, in which the bottom T-layer is saturated with silica atoms in order to avoid unnecessary charges. In the following, we refer to this modified T-layer as a $T^\ast$-layer. Subsequent TOT-layers, below the $T^\ast$-layer, were not taken into account. Charges in the octahedral layer are also ignored.

In order to obtain the complete TOT*-layer electrically neutral, monovalent cations where placed for compensating onto the negative top layer (T-layer). A simple sketch of our structure can be seen in Figure 4.1.

4.2.2 Force field

We have used common clay potentials from the commercial force field cvff$^{[13]}$. This force field only considers pairwise Coulombic and van-der-Waals interactions between nonbonded atoms in the following way:

$$E_{\text{nonbonded}}^{ij} = \sum_i \sum_j \left( \frac{a_{ij}}{r^2} - \frac{b_{ij}}{r^6} + \frac{q_i q_j}{4 \pi \varepsilon_0 r} \right)$$

(4.1)
Figure 4.1 Simplified representation of the mica surface from the natural mica structure (left) to the modified mica layer bearing the T* layer below the O layer (right).

where $a_{ij} = \sqrt{a_{ii}a_{jj}}$ and $b_{ij} = \sqrt{b_{ii}b_{jj}}$, $\varepsilon_0$ is the dielectric permittivity of vacuum, $r$ the interatomic distance, and $q_i, q_j$ are the partial charges of the atoms $i, j$. Potentials for the organic cations were derived from the cvff force field [14-15]. The force field parameters are listed in Table 4.1.

### Table 4.1
Potential types, partial charges, and nonbonded interaction parameters as used in the molecular dynamics simulation

<table>
<thead>
<tr>
<th>atom/ion</th>
<th>partial charge</th>
<th>12-6 LJ parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$ (repulsive)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (attractive)</td>
</tr>
<tr>
<td></td>
<td>$\text{(kcal mol}^{-1} \text{Å}^2)$</td>
<td>$\text{(kcal mol}^{-1} \text{Å}^6)$</td>
</tr>
<tr>
<td>Al (in T-layer)</td>
<td>1.4</td>
<td>183.7928</td>
</tr>
<tr>
<td>Al (in O-layer)</td>
<td>1.4</td>
<td>2326.0964</td>
</tr>
<tr>
<td>O</td>
<td>-1.2</td>
<td>989199.2750</td>
</tr>
<tr>
<td>H</td>
<td>1.0</td>
<td>0.0046</td>
</tr>
<tr>
<td>Si</td>
<td>2.4</td>
<td>368.5103</td>
</tr>
</tbody>
</table>
Table 4.1
Potential types, partial charges, and nonbonded interaction parameters as used in the molecular dynamics simulation

<table>
<thead>
<tr>
<th>atom/ion</th>
<th>partial charge</th>
<th>12-6 LJ parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( a ) (repulsive) (kcal mol(^{-1}) Å(^{12}))</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>1.0</td>
<td>1154.3029</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1.0</td>
<td>224513.0317</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1.0</td>
<td>12886.4561</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>1.0</td>
<td>4300534.1423</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>1.0</td>
<td>7280468.2656</td>
</tr>
<tr>
<td>O (water)</td>
<td>-0.82</td>
<td>629358.0000</td>
</tr>
<tr>
<td>H (water)</td>
<td>0.41</td>
<td>0.00000001</td>
</tr>
</tbody>
</table>

Aluminium atoms can be found in different electrostatic environments in the surface and one has to distinguish between aluminum coordinated to four oxygens in the tetrahedral layer and aluminium coordinated to six oxygens in the octahedral layer. This is reflected in considerably different potentials for aluminum in the two types of environment. The parameters used for the alkaline ions are individually optimized for their most important salts and, since different anions were considered in the force field’s construction for the different ions, they lack systematic trends in the Lennard-Jones parameters with atomic weight. Potential parameters, other than those for clay atoms, are taken from an earlier force field, cvff, for consistency. As a simple test for the force field, the muscovite mica structure from the Cambridge Crystallographic Database was subjected to a fixed-box-shape MD run (“NVT”) for 200 ps. The structure proved to be stable and to display a maximum mean displacement of the atoms from the database coordinates of ca. 0.2Å.
4.2.3 Simulation systems and cells

This section gives an overview of the simulation systems employed (Figure 4.2).

System 1 represents a single mica TOT* layer and alkaline counterions in vacuo. System 2 comprises, in addition, a 12-13 Å thick water layer on top of the T-surface with an initial density of 1 g/cm³. The replacement of at least one of the inorganic alkali surface ions by organic cations leads from System 1 to System 3 (in vacuum) and analogously from System 2 to System 4 (with a water layer).

Figure 4.2 Model systems for the simulations. 1: Inorganic ions on the surface in vacuo; 2: water-covered muscovite mica-surface; 3: same as 2 but after ion exchange of an inorganic ion; 4: same as 3 but with a surface covered with water.
Unless noted otherwise, we employ a computational box of four unit-cell replicates of mica in the direction of the crystallographic a-axis (x), three unit-cell replicates in the direction of the crystallographic b-axis (y), and one single TOT* mica layer of 10 Å in the z direction. As illustrated in Figure 4.2, the mica layer is placed in the box with the T* layer towards the negative z direction. During MD-simulation, the atoms of the mica structure are kept fixed in space. The origin of the coordinate system in z direction is set to the mean position of the top most oxygen atoms of the muscovite layer. For the purpose of illustrations, the mica layer is always shown “at the bottom” of the box. For technical reasons, Ewald summation\textsuperscript{16} can only be applied in three dimensions. Since our systems have two dimensional periodicities in the x,y-plane but are aperiodic in the z direction, we chose a simulation cell size in the z direction many times the possible range of calculated interactions i.e., ca. 100 times larger than in the x and y direction. In Systems 3 and 4, the water was assembled as a compact layer under vacuum. During MD simulations, these water layers display normal local mobility and are stable, i.e., no water molecules vanish into the vacuum and the density of the water near the surface remains at its bulk value except for a layer of 2-3 Å at the interface to the vacuum (see below).

### 4.2.4 Simulation details

Molecular dynamics simulation were performed in the NVT-ensemble (fixed box shape). The number of atoms was between 492 (System 1) and ca. 2000 (System 2 and 4). Spacial continuation conditions were taken into account using Ewald summation for the Coulombic interactions. As integrator, the Velocity-Verlet algorithm was used. The time step during simulation ranges between 1 and 2 fs and the temperature was controlled using velocity scaling. Usually, we sampled configurations along the MD trajectory for 100-150 ps. A typical snapshot of a molecular dynamics simulation with a thin film of water covering the muscovite mica can be seen in Figure 4.3.
4.3 Results and Discussion

4.3.5 Where are the counterions? - ions on a rigid arrangement (no H₂O)

On a dry muscovite surface, the inorganic ions interact with the muscovite surface by Coulombic- and van-der-Waals potentials. At the internal surfaces, these ions stay in a cavity surrounded by silicon, aluminum, and oxygen atoms. As a first step, we determine the nonbonded interaction energy in vacuum (System 1, Figure 4.2) of inorganic cations, such as lithium, sodium, potassium, and cesium ions, by calculating the nonbonded interaction potential of one probe ion with the system. Except for this ion, all other atoms and ions are kept fixed in their pre-assigned location (see Figure 4.4).
Figure 4.4 Sketch of the simulation cell for the simulation of inorganic ions in vacuo.

The probe cation is placed on the vertices of a three-dimensional cubic grid (lattice constant 0.5 Å) over the surface and the interaction energy with the system is calculated (see Eq. 2). The probe ion was formed to have one strongly favored position above the lattice. In order to visualize the energetic situations, the following procedure was applied: we determined the minimum of the interaction energy along the z-direction (perpendicular to the surface) and use these minima in the x,y-plane (the muscovite surface) to construct a minium-energy surface $E_{\text{min}}(x,y)$ (Figure 4.5).

The minimum-energy profile, on top of Figure 4.5, is calculated for a system with a TOT layer of 9x9x1 unit cells (9 each in x and y direction), whereas the lower potential energy surface is calculated for a mica sheet of 3x3x1 unit cells. The x and y axes are parallel to the crystallographic a and b axis, respectively. Evidently, the minium energy surfaces contain a global minimum of $E(x,y,z)$ each at the same x,y position on the mica surface. In the vicinity of this minimum, $E_{\text{min}}(x,y)$ increases by at least 10 $k_B T$ within less than 1 Å², as can be derived from the contours drawn in Figure 4.4 ($k_B$ is the Boltzman constant and $T$ is the absolute temperature).
A displacement of 2 Å requires more than $50 k_B T$ which seems to be quite impossible for the alkali ions to "top" over the surface. These ions are retained in their minimum positions, strongly bound and immobilized. Analogous results are obtained for the other alkali ions. They all show strong confinement. A simple estimate of the rms displacement at 300 K yields $\langle \Delta x^2 \rangle^{1/2} = \langle \Delta y^2 \rangle^{1/2} \sim 0.2$ Å.

The depth of the potential energy trough at a fixed x,y position when moving along z is on the order of -130 kcal/mol. (-130 for Li⁺, -116 for Na⁺, -143 for K⁺, -95 for Rb⁺, -80 for Cs⁺ at $x = y = 0$), i.e., in the order of a covalent bond. It is evident, then, that exchange of the surface ions must involve a concerted action of an incoming and a leaving ion,
rather than a random abstraction of an ion from the surface and the subsequent uncorrelated arrival of the new ion.

4.3.6 Muscovite surface covered with water and inorganic ions in a flexible arrangement

In System no. 2, the muscovite surface 4x3x1 unit $TOT^*$ cells is covered with lithium counter ions and a layer of 233 water molecules 12-13 Å in thickness. In our setup with a $z$ direction of ca. 2000 Å (see above), the water layer is "sandwiched" between a rigid surface of substantial high electrostatic potential and vacuum. Remarkably, the water layer, initially placed as a regular lattice of H$_2$O molecules with a density of 1 g/cm$^3$, rapidly relaxed with time in MD simulations (structural relaxation time of ca. 5 ps) but remained a compact sheet of water for the entire simulation (up to 100 times the structural relaxation time). No H$_2$O molecule was observed to leave the surface and "escape" into the vacuum. The density at the surface was not the same as in the "bulk", however. We plotted the density and cohesive energy of the water molecules layerwise with increasing distance from the surface by averaging over 50 snapshots along the MD-trajectory (every ps) (Figure 4.6). The density is calculated by counting all H$_2$O whose oxygen center lie in a given $z$ interval (size 1 Å), i.e., in a slice of 1 Å parallel to the surface.

In analogy to the density, the nonbonded interactions of a water molecule with all atoms in the system were computed.

Figure 4.7 displays the averaged layerwise interaction energy $\langle E_{nb}(z) \rangle$ with increasing distance $z$ ($\Delta z = 1\text{Å}$) perpendicular to the surface. Also drawn are the simulated bulk value (for a liquid-water system in an NpT simulation at 1 bar and 300 K) and the experimental bulk value, i.e., the cohesive energy.

The layerwise density and interaction energy, respectively, can be divided into three main regions. The first region near the solid surface ranges from $z = 0$ Å to $z = 4$ Å and will be termed the interfacial region. Here, the water molecules are strongly bound to the surface, as it can be derived from the substantially negative interaction. The density in this region is higher than in the bulk. The second region, ranging from 4 Å above the
surface to 12 Å, parallels the behavior of bulk water. Within the statistical error, the

interaction energy and the density are equivalent to the values obtained experimentally
for the bulk \(^{[17]}\). The third region, for \(z > 12 \text{ Å} \), forms the interface between the bulk
water and vacuum with lower density and interaction energy.

The rapid loss of specific surface effects with increasing \(z\) might be surprising. It could
be rationalized by a rough estimate of the thickness of the Stern-layer\(^{[18]}\). The inorganic
ions on the surface represent, in these systems, the so called first Stern-layer. Using the
Boltzmann-Poisson equation for the charge distribution away from a single surface

\[
\rho_S = \frac{\sigma^2}{2\varepsilon\varepsilon_0 k_B T}
\]  

where \(\sigma\) is the surface charge density, \(\varepsilon\) is the relative dielectric constant for the solvent,
\(\varepsilon_0\) is the permittivity in vacuum, \(k_B\) is the Boltzmann constant and \(T\) the absolute

Figure 4.6 Averaged layerwise density with distance from the surface. The error bars
indicate the standard deviations of the distributions. The dotted lines show the exper¬
imental values for bulk water at 1 bar and 300 K. The value where \(z = 0\) refers to the \(z\)
coordinate of the topmost oxygen atoms in the muscovite mica layer.
Figure 4.7 Average layerwise interaction energy of a water molecule with all other atoms in the system. The horizontal lines mark the cohesive energy of the bulk water from a simulation at 1 bar and 300 K (dot-dashed) and from experiment at the same conditions (dotted).\textsuperscript{17}

Using typical values for the mica surface, i.e., $\sigma = 0.343$ C/m$^2$ (one charge per 46.7 Å) at 300 K, one obtains a value of

$$\rho_S = 2.01 \times 10^{28} \frac{1}{\text{mol} \cdot \text{m}^3}$$  \hspace{1cm} (4.3)

Muscovite mica contains one charge per 45 Å$^2$. Together with $\rho_S$, this leads, subsequently, to a layer thickness above the negatively charged surface of ca. 1 Å in water, where $\varepsilon = 80$.\textsuperscript{3} From this result, we conclude, that due to the electrostatic interactions of surface and surface ions, the electrostatic potential drops to zero within a few Angstroms.

It can be seen that the simulations faithfully mimic the surface covered with solvent molecules, spatially periodic in two dimensions, to a distance of 12 Å above the surface conditions and the simulation model can be applied for this kind of simulations. Below a critical distance, the system is considered as a surface covered with solvent molecules with periodicity in two dimensions in which both regions, the bulk region and the interfacial region, can be investigated.
We have shown in the sections above that inorganic ions are strongly localized on the surface. The probability for finding an ion at a given location is obtained here independently for the $x$, $y$, and $z$ coordinate and is plotted for Li$^+$ in a System 2 configuration with 233 water molecules in Figure 4.8. Clearly, the confinement of the ions at 298 K is distinct, as has been expected from the simple calculations in vacuum in our System 1 simulations. For the other alkali ions, the relative location probabilities in $x$ and $y$ direction (in the plane of the surface) are nearly the same. The same is not true for $P(z)$, perpendicular to the surface. The plot in Figure 4.8 (top) shows that the lithium ions are penetrating to some extent into the pits on the mica surface.

![Figure 4.8](image)

**Figure 4.8** Probability distribution for the location of lithium ions on muscovite mica (265 water molecules, 300 K). $\Delta x = \Delta y = \Delta z = 1$ Å.

The top plot in Figure 4.9 presents the same data for the $z$-direction. Sodium and potassium ions are common counter ions in minerals and might be expected to exhibit the strongest interactions with the surface ("fit best into the surface pits"). Indeed, the probability distribution in $z$ direction for those ions reveals a maximum shifted by ca. 0.5...
Å, relative to that of lithium towards the muscovite surface. A significant fraction of these ions is actually below the level of the topmost mica oxygen atoms! Rubidium and cesium ions do not seem to fit well into the surface pits and are located further from the surface, as can be seen in Figure 4.9. The maximum displacement of any alkali ion, during the molecular dynamics simulations, was less than 1 Å at 300 K, since only a slightly narrower distribution is obtained for a surface in vacuum, the effect of water molecules on the energetics and mobility of these inorganic surface ions seems to be negligible.

![Figure 4.9](image)

**Figure 4.9** Probability distribution for the distance from the surface, $P(z)$, for all alkali surface ions. The arrow emphasizes that $z = 0$ is the level of the topmost oxygen atoms in the muscovite mica structure.
The pair-distribution function $g(r)$ for water-oxygen atoms with alkali ions and for water-hydrogen atoms with alkali ions shed light on the orientation of water molecules surrounding the surface ions. They are drawn for $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$ and $\text{Cs}^+$ in Figure 4.10; $I^+$ refers to the alkali ion. All $g(r)$ display the same typical behavior: a strong population for oxygen and hydrogen atoms of water molecules near the ions result from the first hydration shell. The maximum of $g(r)$ for oxygen is nearer to the inorganic ions than the one for hydrogen due to the electrostatically motivated orientation of $\text{H}_2\text{O}$ around the ions. In the case of lithium, evidence for a second hydration shell can also be observed. With increasing size of the alkali ion, the distance between the first maxima for oxygen and for hydrogen diminishes, probably due to a decreased strength of the electrostatic interactions between the larger ions and water.

![Figure 4.10](image)

**Figure 4.10** Pair distribution function for $I^+/\text{oxygen}$ and $I^+/\text{hydrogen}$ in water, where $I^+$ refers to the surfaces cations: $I^+ = \text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Cs}^+$. The dashed line corresponds to the equilibrium distance $\text{Li}^+-\text{water oxygen}$. The left sharp peak indicates the $I^+-\text{O}$ distance whereas the right peak indicates the $I^+-\text{H}$ distance.
The maximum distances between the first oxygen and hydrogen atoms is shown in Table 4.2.

<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>g(O-I⁺)</td>
<td>2.12</td>
<td>2.34</td>
<td>2.57</td>
<td>3.23</td>
</tr>
<tr>
<td>Δr¹</td>
<td>0.63</td>
<td>0.64</td>
<td>0.65</td>
<td>0.63</td>
</tr>
</tbody>
</table>

¹ Δr is the distance between the two first maxima of g(O-I⁺) and g(H-I⁺).

4.3.7 Organic ions on the surface

Motivated by the experimental study described in Chapter 3 and 6, we analyzed mica surfaces with terminally attached organic cations, specifically poly(ethylene oxide) derivatives containing a positively charged trimethylammonium head group (see Figure 4.11). Note that the head group is considerably larger (effective vdW-radius between 3-4 Å) than those of the alkali cations (effective vdW radii 0.5 - 1.7 Å).

![Molecular structure of the simulated organic molecules. Simulations were carried out for x = 1 and x = 4.](image)
With the "monomer", i.e., $x = 1$, simulations for different grafting densities were carried out. For $x = 4$, only the lowest grafting density of $1/12$ (1 out of 12 alkali ions exchanged) was considered. Due to the bulkiness of the trimethylammonium group, these anchors cannot approach the surface as close as the small inorganic ions. The backbone consists of ethylene oxide repeating units that provide a balance between hydrophobic and hydrophilic behavior.

The probability distribution of location for $x = 1$ and $x = 4$ with a surface coverage of $1/12$ is plotted in Figure 4.13. Here, one inorganic cation on the surface was exchanged by an organic cation and the other 11 inorganic cations remain in their positions. The following probabilities for the location of the nitrogen atom were obtained as those for the alkali ions, after averaging over the MD trajectory and with a resolution of $\Delta x = \Delta y = \Delta z = 0.1$ Å. These distributions are broader in all directions for the nitrogen atom than for the alkali ions. This is due to the larger distance from the surface of the trimethylammonium group and the concomitant decrease in the interaction energies. Nevertheless, these organic ions are immobilized in space by the interactions of the cationic head group with the surface. There is no apparent difference in the breadth of the distribution for the "monomer" ($x = 1$) and the tetrameric chain ($x = 4$).
Figure 4.12 Probability distribution for the location of the nitrogen atom in the head group of the chains with $x=1$ and $x=4$, with a surface coverage $\sigma$ of 8.4% (1 out of 12). Ion exchange of surface ions against organic cations results in a change of the surface.

For example, if the surface is covered with an apolar substance, it becomes hydrophobic. It is, therefore, relevant to study the interactions of the organic molecules with the system in function of the degree of surface coverage, as well as those of the solvent, in parallel. The change in interaction energy for water (cf. Figure 4.7 for alkali ions only) in systems with different surface coverages of the "monomer" is shown in Figure 4.13.

These results were obtained completely analogously to those in the case of alkali cations only. From the values obtained it is evident that the layerwise interaction energy of $\text{H}_2\text{O}$ is essentially unchanged for up to 50%, but the complete organic surface provides a very different environment for the water, however. Even thus, the effect is short-ranged: above the organic layer, at $z > 7 \text{Å}$, the interaction energy of water reaches its bulk value. The layerwise nonbonded interaction energy for one of the grafted molecules is also
displayed in Figure 4.14.

![Figure 4.13](image)

**Figure 4.13** Average layerwise interaction energy of water for different surface coverages with the “monomer” \(x=1\), in function of the distance \(z\) from the surface.

It is striking that the effects in the case of the organic cations are weak, compared to those observed with water molecules. The explanation for this might be that the Coulombic interactions that are important for water, are relatively weak for the organic cations due to the bulkiness of the head group and the fact that the molecules dipole moment are modest. For the treatment of experimental data it will be important to keep in mind that changes in the surface coverage will cause changes in the energetics at the surface and in the surrounding water structure. Changes in the surface coverage will cause changes in the orientation of \(x = 1\) and further changes the surrounding water structure.
4.3.8 Orientation of water and organic molecules near the surface

Water orientation

In order to describe the orientation of water relative to the surface in more detail, we considered all water molecules in the slabs parallel to the surface used to compute the layerwise interaction energy and construct pole figures of vectors fixed in the molecular frame. The construction of pole figures, framed as a vector field, routinely performed in morphological studies, is sketched in Figure 4.15, for easy reference.
The orientation of the vector connecting the hydrogen atoms in H$_2$O at different surface distances is shown in Figure 4.16.

Figure 4.15 Construction of a pole figure: Procedure to obtain an image dot in the image plane for a vector $\mathbf{r}$

Figure 4.16 Layerwise pole figures for the H-H vector in water in slabs of thickness 1 Å parallel to the surface.
The corresponding plots for the dipole moment vectors can be seen in Figure 4.17. The distance intervals are identical to those used in the construction of Figure 4.7 and Figure 4.13.

![Diagram of Layerwise pole figures of the dipole moment vector of water in slabs of 1 Å thickness parallel to the surface.]

Figure 4.17 Layerwise pole figures of the dipole moment vector of water in slabs of 1 Å thickness parallel to the surface.

At first blush it is evident that these distributions are cylindrically symmetric around the z direction; the crystallographic symmetry of the surface has no effect upon the distribution of the dipoles. At very low z values (z < 2 Å), the water molecules are strongly oriented with their hydrogen atoms towards the surface. A search of all structures reveals that no H₂O points with its oxygen towards the surface. The dipole moment is nearly perpendicular to the surface, whereas the H-H vector is situated in the plane of the surface. Water molecules in the next layer (2 Å < z < 3 Å) show a rather random distribution of their orientation, possibly because the solvation of the alkali cations forces some water to orient differently. As a result, no preferential orientation of water molecules can be determined. In the following layer, a bias towards H-H perpendicular to the surface is evident (H-bonds to the first water layer) and the
following layers are randomly distributed

The orientation of the \((\text{CH}_3)_3\text{N}^+\text{-CH}_2\) bond vector and the vector between \(\text{N}^+\) and \(\text{O}\) can be analyzed in the same way. These vectors describe the orientation of the head group and the first chain segment, respectively. Figure 4.18 displays the distribution of the angle between the vector and the \(\text{z}\) axis, for the case of the \(\text{N}^+\text{-CH}_2\) bond.

**Figure 4.18** Angle of the N-CH\(_2\)-vector with the \(\text{z}\)-axis at different surface coverage as indicated in the Figure. No. 1: 8.3\%, No. 2: 25\%; No. 3: 50\%; No. 4: 100% coverage with \(x = 1\).

At low coverage, the “monomer” \((x = 1)\) exhibits a tendency towards “lying down” on the surface. With increasing \(\sigma\), the N-CH\(_2\) bonds begin to favor more “upright” orientation. Since the monomeric unit enjoys a considerable conformational freedom, the vector between \(\text{N}^+\) and the oxygen at the methoxy group might show a different behavior (Figure 4.19 displays a sketch of two conformations). Figure 4.20 shows the distribution of \(\zeta\) for the vector between \(\text{N}^+\) and \(\text{O}\). Clearly, at low coverage, the chains tend to lie flat on the surface (as in Figure 19a) while at high surface coverage they tend to “stand up”.
One might speculate that the chains, and especially the chains, and especially chains, and especially the methoxy group, favor interactions with neighboring alkali ions at low coverage, whereas such interactions cannot be established in a more crowded case. Therefore, a more upright orientation is favored for these cases.

**Figure 4.19** Two conformations of the “monomer”, both with a N\(^{+}\)-CH\(_2\) bond perpendicularly to the surface but the one in a) lying flat on the surface, and the one in b) standing “upright”.

**Figure 4.20** Distribution of the angle between the vector N\(^{+}\)-methoxy O for different surface coverage of the “monomer”.
The time-autocorrelation function of the N-CH$_2$-bond vector was analyzed to ascertain that sampling of the relevant configuration space was guaranteed. It was found that the orientational relaxation time was less than 5 ps for all systems. During a typical molecular dynamics run of 150 ps, configurational space is explored sufficiently. The "end-to-end" vector (N-O) disorients only marginally slower.

4.4 Conclusions

To summarize our results, we draw the following conclusions:

1.) All alkali cations and the trimethylalkylammonium cations investigated are highly localized near their equilibrium position, if they are stoichiometrically required to balance the surface charges.

2.) The degree of confinement of the cations varies strongly with the type of ion. For alkali ions, the effect is largest along the z-direction, other cations differ also in the in-plane confinement. This can explain substantial differences in the exchange-equilibrium constants of different ions.

3.) The orientation of the head group is significantly dependent on coverage (but not on DP)! Also, the interaction energy depends on the coverage in this case. This means that in comparison systems with different DP must be compared at the same surface coverage!
References


[12] Crystal data: monoclinic symmetry group C12/C1, with Z = 4, a = 5.194Å, b = 8.996(6)Å, c = 20.096(2)Å, α = 90.0,β = 95.18, γ = 90.


5. Polymer Brushes: Experiment and Theory

5.1 Introduction

In view of the technological applications, understanding the equilibrium and dynamical interfacial properties of polymer brushes, grafted at one end at a liquid-solid interface is one of the most important topics in surface science. Most systems deal with either chemisorbed or physisorbed chains. Within the framework of those two grafting methods, it is difficult to study the thermodynamic properties of polymer brushes. The limitations are on one hand that chemically-bound chains cannot stay in dynamic equilibrium with polymers in solution. On the other hand, physisorbed chains are difficult to analyze with respect to their bound fraction. Such experiments have to be performed in solution with IR-, NMR-, ESR-spectroscopy\[^{12-8}\] or other experimental methods.

To study the polymer brush formation and the related thermodynamical properties, the following requirements must be met:

1. The polymer chains on the surface must stay in dynamic equilibrium with the polymer chains in solution. This is the most important condition the system has to fulfil. Only from equilibrium conditions, the free energy differences can be determined.

2. The grafting mode is well known. This means that the behaviour of the chain on the surface and the way in which the polymer is attached to the surface is known. It is most favourable if the polymer contains a well characterized grafting point at the end of the chain and the tail of the chain shows no interactions with the surface in contrast to the head group.

3. The surface area of the substrate can be measured exactly or is well known.
4. The grafting density of the polymer on the surface can be determined with high precision.

5. By varying system parameters it should be possible to change adsorption behaviour.

Polymer brush formation via ion exchange offers a method that combines all the necessary parameters that have to be taken into account for an experimental model system to study polymer brushes. In addition, ion exchange offers an excellent method to prepare polymer brushes by performing the reaction in solution. The equilibrium between the polymer at the surface and polymer in solution is established after a certain period of time and the samples can easily be worked up to determine experimentally the amount of end-grafted polymers on the surface. This method allows one to determine equilibrium properties with high accuracy and serves as an experimental system to measure the free energy of polymer adsorption. As previously shown, in Chapter 2, cation-terminated poly(ethylene oxide) adsorbs on flat inorganic surfaces, such as mica surfaces, via ion exchange reaction and forms a polymer brush. This polymer was end-functionalized with a quaternary, cationic trimethylammonium group. The inorganic surface used was modified in order to increase the specific surface area and to increase the adsorbed amount per gram of mica powder. Thus, the experimental error is strongly reduced. The ion-exchange reaction conditions can be varied by changing system parameters such as temperature and the type of solvent.

Many people have worked with PEO on mica and other surfaces investigating the “in situ” behavior of these chains using sophisticated analytical methods. Properties, such as the volume fraction of the brush using small angle neutron scattering (SANS)\textsuperscript{[9]} or neutron reflectivity\textsuperscript{[10]} have been determined in those cases. The volume fraction profiles can be obtained using neutron scattering but not the surface coverage densities. Despite the fact that there are a lot of experiments using the PEO/water/SiO$_2$-system\textsuperscript{[11]-[13]}, our end-group-modified system offers a new way to calculate equilibrium adsorption
data using experimental values. We use PEO because of its manifold desirable properties such as an excellent solubility in water and organic solvents\(^{[14]}\). It is interesting to note that, due to the broad range of solvents available for PEG, the solvent quality for the ion-exchange reaction can be changed offering the possibility of measuring the equilibrium properties with modified solvent-solute interaction energies.

We present here a theoretical treatment of the polymer brush formation of monocationic polymers on charged organic surfaces via ion exchange. Using the analytical SCF method\(^{[13][15]}\), we described the equilibrium reaction by calculating the chemical potential for each component in solution. For a review on polymer adsorption theories, especially in the case of self consistent field methods and characteristics, see ref. 16. As a prerequisite, the surface coverage density must exceed the value in the cross-over regime. This regime is called the dense brush regime. Within this regime, in which the chains are stretched away from the surface and do not form isolated mushroom spots on it, the SCF theory were believed to be appropriate to calculate free energies of the brush on the surface. Analytical SCF theories are also developed for different kinds of surfaces, either curved or flat, and it is customary to use them for the treatment of polyelectrolytes grafted to surfaces. In these cases, the Debye-Hückel and the Boltzmann-Poisson approximations are augmented, respectively\(^{[17]}\). In this paper, we do not consider any of these approximations, although we are dealing with a charged surface and the release of inorganic ions from it. We assume that our chains are fixed at the surface, bound by strong Coulombic interactions. The modelling results and theoretical calculations of the interaction between ions on the mica surface are shown in Chapter 3. They indicate that even with a water coating of mica particles, the ions are almost fixed in their surface cavities. To test the applicability of other models, we compare our experimental results to theoretical models developed at the end of the 1970’s. During that time, Alexander developed a scaling approach to describe the behavior of end-grafted polymers at interfaces with different kinds of interaction\(^{[18]}\). The chains are supposed to be fully stretched away from the interface with a uniform monomer density. This model is well known as the “step-function” model. Another approach is described by Murat and Grest\(^{[19]}\). They applied molecular dynamics simulation to polymers attached with one end to the surface. They varied the grafting
densities, the polymer chain length, and the solvent qualities. The solvent quality, and therefore the nonbonded interactions of solvent with solute, was modelled by varying the simulation temperature from their molecular dynamics simulation at various grafting densities and chain lengths lead to an expression for entropy. These values will be compared with the experimental results.

The outline of this Chapter is as follows: First, we calculate chemical constants for different chain lengths as used in the experiment in Chapter 2. Then, we derive expressions for the chemical equilibrium constant $K$ and the entropy change, based on self-consistent field methods and other models. After comparing theoretical methods to experimental results, we focus in detail on our self-consistent mean field approach for polymer brush formation via ion exchange.

5.2 In which regime are the experimental results?

For the past 30 years, there has been growing interest in the development of methods for surface modification. This tendency was, and still is, motivated by the increasing possibilities and challenges in the areas of colloid stability and adhesion. Since the great work of S.F. Edwards, a lot of scientists have developed sophisticated methods to describe the behavior of polymers on surfaces. The applicability of those is limited to the ansatz used for describing the polymer brush behavior. Whereas the de Gennes scaling theory\cite{20} is supposed to be accurate within the dilute brush region, the Alexander-de Gennes theory\cite{18} is only applicable in the dense brush regime, where polymers are strongly stretched and their configurational entropy is reduced at the expense of a high osmotic pressure in the brush region. It is therefore necessary to define the polymer brush with respect to its grafting density. The grafting density in comparison with the radius of gyration is one of the main parameters to describe regions in which the polymer brush fits. After determination of the regime, we are able to judge which theory can be used to describe the brush and to derive free energy parameters. A sketch of the three main regimes that a polymer brush can adopt is shown in Figure 5.1.
isolated polymers: \( \langle D \rangle \gg R_g \)
(mushroom)

cross-over regime: \( \langle D \rangle = R_g \)

dense brush regime: \( \langle D \rangle \ll R_g \)

Figure 5.1 Different regimes of a polymer brush as the grafting density increases on the surface

The applicability of these theories is tested using the following experimental data from Chapter 2.

As mentioned above, the self-consistent mean field (SCMF) methods become inaccurate for the description of polymer brushes in the low coverage region, as does the Alexander-de Gennes theory for stretched brushes. At that point, where the chains start to overlap, we enter the cross-over regime, in which the chains begin to contact each other. With increasing grafting density, the chains must stretch normal to the surface loosing configurational entropy due to limited orientation possibilities, but they gain free energy from grafting of the endgroups.

The point at which the cross-over occurs can be determined in the following way. The radius of gyration \( R_g \) of an unpertubed polymer in solution can be expressed as:

\[
R_g = \frac{1}{\sqrt{6}} L \left( C_\infty n \right)^{\gamma}
\] (5.1)
where $L = 0.15 \text{ nm}$ is the effective bond length, $C = 4$ is the characteristic ratio and $\gamma$ is a solvent quality parameter\textsuperscript{[21]}. This value is equivalent to 0.5 for a theta solvent and 0.6 for a good solvent, where the chain is supposed to be more swollen than in the theta state.

The factor $n$ determines the polymerization index including the number of bonds. This can simply be calculated by

$$n = 3x + 1$$

in the case of poly(ethylene oxide). Despite that the polymer has access to only a half of the configurational space due to end-grafting to the impermeable surface, we assumed that in the very dilute case the radius of gyration is roughly the same as in solution. Then the cross-over surface coverage $\Gamma_a^*$ can be calculated according to

$$\Gamma_a^* = \frac{S}{\pi R_g^2} \cdot \Gamma_{a, \text{maximum}}$$

where $S$ refers to the unit cell area and is, in the case of muscovite mica, equivalent to 45 Å$^2$, as shown in Figure 5.3.

![Figure 5.2 Sketch of a polymer covered mica surface with $R_g$ to the radius of gyration. The way to calculate the surface coverage is described in the text.](image-url)
The value $\Gamma_{a, \text{maximum}}$ refers to the plateau value in the adsorption isotherm. The cross-over surface coverage determines the number of polymers per unit surface area, at which the polymers begin to overlap. We have calculated this value for the case of a good solvent and a theta solvent.

Depending on the temperature, water is considered to be a good solvent for poly(ethylene oxide). In our case, we assume that water ranges between a good solvent and a theta solvent because of the release of counterions from the surface. This influence reduces the solvent quality of water\textsuperscript{[14][22]} to some extent. The cross-over values are listed in Table 5.1 as calculated from eq. 5.3.

**Table 5.1**

<table>
<thead>
<tr>
<th>$x$</th>
<th>theta state ($\gamma = 0.5$)</th>
<th>good solvent ($\gamma = 0.6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>0.23 (0.45)</td>
<td>0.08 (0.45)</td>
</tr>
<tr>
<td>117</td>
<td>0.1 (0.25)</td>
<td>0.03 (0.25)</td>
</tr>
<tr>
<td>234</td>
<td>0.014 (0.1)</td>
<td>0.003 (0.1)</td>
</tr>
</tbody>
</table>

In parenthesis, we have indicated the plateau values of adsorption depending on the polymerization index $x$. In every case, the cross-over point is either half the value of the maximum possible amount of polymer or lower than the maximum value. With increasing molecular weight, the cross-over point further drops to a value of ca. 10% of the maximum exchange capacity with the polymer in the case of $x = 234$.

For this reason, we are sure of being at least in an overlapping regime with our model system, even at low amounts of polymer in solution. With increasing amount of polymer in solution, we can cross the threshold of the overlapping regime toward the formation of a dense brush system. As a consequence, we can investigate the regimes in which self-consistent mean-field method should be applicable. Using the SCF method, as developed by Milner et al. (1987), the amount of polymer on the surface should scale with the degree of polymerization $x$ as follows.
where \( c \) is a constant. In the following, we show that this relationship is indeed fulfilled and the self-consistent mean-field method is suitable to describe our experiments.

5.3 The chemical constant and entropy

In the preceding section, we have described our experimental system and explained the conditions that have to be fulfilled for derivation of free energy values of the system. The reaction, can easily be written as

\[
P(l) + I(s) \rightleftharpoons P(s) + I(l)
\]

where \( P \) refers to the polymer and \( I \) to the small ions on the surface. The parameters \( l \) and \( s \) refer to the liquid and to the grafted state, respectively.

A sketch of the process of polymer brush formation via ion exchange can be seen in Figure 5.3.

**Figure 5.3** Sketch of the ion-exchange adsorption of a cation-terminated polymer on an inorganic surface containing surface cations.
For the polymer, the changes in free energy for this reaction can be written as

\[
\frac{\Delta \mu_{\text{polymer}}}{kT} = \frac{\Delta \mu_{\text{head}}}{kT} + \frac{\Delta \mu_{\text{tail}}}{kT}
\] (5.5)

The change in free energy for this reaction can be divided into two parts. One part is the change in free energy due to bringing the headgroup from solution to the surface, and the other part is the change in free energy of the tail of the polymer due to changes in configurational space of the confined polymer at the interface. The first addend mainly is an enthalpic function. While the polymer performs its adsorption reaction, the Flory-interaction parameter does not change, at first glance, and therefore, the changes in the enthalpic part of the last addend cancel. What remains is an entropic part. The first addend can be determined by performing the ion-exchange reaction only with the headgroup of the polymer. This molecule refers to \( x = 1 \). The change in free energy of the complete system can also be determined. Therefore the tail-free energy can be calculated as follows:

\[
\ln \frac{K_{\text{polymer}}}{K_{\text{head}}} = \frac{\Delta \mu_{\text{tail}}}{kT} = \left( -\frac{\Delta S_{\text{tail}}}{k} \right)
\] (5.6)

The difference on the right side of eq. 5.6 can be determined experimentally. Therefore changes in entropy for the tail part of the polymer can be calculated as a function of the chain length. For the calculation of equilibrium constants, we perform a fit with the following equation, that was derived by Caseri et al.\textsuperscript{[23]}

\[
K = \frac{\Gamma_s^2}{[S - \Gamma_a][a - \Gamma_a]}
\] (5.7)

where \( S \) is the maximum possible exchange capacity with the system, \( a \) is the amount of polymer in solution per unit area accessible surface and \( \Gamma_a \) is the amount of polymer on the surface per unit surface area. Usually, the unit of these values is expressed in \( \mu \text{mol/m}^2 \). Fitting eq. 5.7 to the experimental data, using a nonlinear least-square Levenberg-Marquardt algorithm, we obtain the chemical constant \( K \) and the maximum exchange capacity \( S \). Remember, the maximum exchange capacity \( S \) is a constant and only changes with the type of surface used.

Inserting the equilibrium constants \( K \) in eq. 5.6, we derive the chain-length-dependent
entropy changes for the polymer adsorption. These values are listed in Table 5.2.

\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{x} & \textbf{K} & \textbf{\(\Delta S_{\text{tail}}/k\)} \\
\hline
1  & 0.9959  & 0     \\
47 & 0.0034  & -5.68 \\
117 & 5.87 \cdot 10^{-4} & -7.44 \\
234 & 1.47 \cdot 10^{-5} & -11.12 \\
\hline
\end{tabular}
\caption{Fitting with the simple model system: water, 33°C.}
\end{table}

For the case of \(x = 1\), the ion exchange constant appears to be very close to unity, a result anticipated by the fact that lithium and tetramethylammonium have very similar hydrated sizes either in solution and on the surface. The entropy change for adsorption of the polymer is negative. This is expected from the limited configurational space on the surface.

5.4 Self-consistent mean field theory for polymer adsorption via ion-exchange

This section, we intend to briefly present a self-consistent mean field method, which is based on the theory originally developed by Milner\(^1\), and further extended by Ligoure and Leibler\(^15\).

The main idea that comes out of that theory is that the potential, in which the chains find themselves, can be described as an equal-time potential. The volume fraction profile is determined by the potential that is on the other hand determined by the volume fraction profile of the chains. The solution of this system, i.e., the determination of the volume fraction profile can be derived self-consistently.
The current system of interest can be described in terms of a simple ion exchange reaction of one cation against another. After a certain time, the system reaches equilibrium. For this ion exchange reaction, one can write the following Gibbs energy:

$$\Delta G_R = \sum_i v_i \cdot \mu_i$$  \hspace{1cm} (5.8)

where $v_i$ is the coefficient in the equation for the chemical reaction of the component $i$ (P or I) and $\mu$ is the chemical potential, respectively.

The following equations are developed with respect to a model, where the size of a solvent particle and also the size of a small ion $I$ is equivalent to the Kuhn length $l$. Therefore, we can write the contour length $A$ of a polymer chain P as $A = lx$, where $x$ is the polymerization index.

For the solution of eq. 5.8, one needs to know the chemical potential of each participant in the reaction. The theory for equilibrium electrochemistry provides us with the equation for the chemical potential of ions in solution:

$$\frac{\mu_{I(l)} - \mu_{I(0)}}{kT} = \ln \Phi_{I(l)} + \zeta_{I(l)}$$  \hspace{1cm} (5.9)

where $\Phi_{I(l)}$ is the volume fraction of ions in solution and $\zeta_{I(l)}$ is a dimensionless contribution due to electrostatic interactions in solution affecting the chemical potential of the ions. The last term in eq. 5.9 can be calculated using the Debye theory for dilute solution.

For the chemical potential of the ions on the surface, we can write the following term, which describes the electrochemical potential of ions bound to an ionic surface.

$$\frac{\mu_{I(s)} - \mu_{I(s)}}{kT} = \ln \sigma_{I(s)} + \Delta_{I(s)}$$  \hspace{1cm} (5.10)

where the first term is the surface coverage $\sigma = I^2 / \Sigma$ ($\Sigma$ is the available surface area per chain) and the last term on the r.h.s is a dimensionless electrostatic interaction parameter that gives a contribution to the interaction of the ions with the surface in the first Stern layer. We only consider ions bound to the surface in the first Stern layer. Non-bound ions refer to ions in solution. With the equations above, we tried to be consistent with the notation used in ref. 15.

Furthermore, it is necessary to develop the chemical potential of a polymer terminally attached to the surface. This Gibbs energy is derived directly from the analytical self-
consistent mean field theory. What we want to show here is that SCF can be applied in a reasonable sense for understanding the ion exchange with our cationic terminated polymers. In our case, the free energy of the brush contains two contributions

\[
\frac{G_{P(s)}}{M} = G_{el} + G_{\text{head}} + kT\ln\sigma_{P(s)}
\]  

(5.11)

namely one from the elastic deformation \(G_{el}\) of the chain due to entropic penalties, and another one \(G_{\text{head}}\) due to the free energy gain upon electrostatic interactions with the surface of the ionic head group. \(M\) is the number of chains attached to the surface. Milner describes the chemical potential of a polymer chain by an analogy of the diffusion of a quantum particle in an equal time potential \(U(z) = A(\sigma_{P(s)}) - Bz^2\), where \(A(\sigma)\) is the potential energy that a polymer feels at \(z = 0\). The difference in the free energy of the system, upon adding a chain to an already existing brush, is defined as \(s(\sigma_{P(s)})\). Because \(s(\sigma_{P(s)})\) is derived within an equal time potential, the free energy difference \(s(\sigma_{P(s)})\) does not depend on the positions of the free ends of the polymer chains terminally attached to the surface. The variable \(z\) is set to zero and the potential energy \(U(z)\) can be written as \(U(0) = NA(\sigma_{P(s)})\), so that \(s(\sigma_{P(s)})\) becomes equal to \(NA(\sigma_{P(s)})\) where \(N\) is the polymerization index. The elastic free energy of the chains can now be easily derived by just integrating over the surface coverage \(\sigma_{P(s)}\).

\[
\frac{G_{el}}{kT} = \int_{0}^{\sigma_{P(s)}} s(\sigma') d\sigma'
\]  

(5.12)

The second term in eq. 5.11 can be written as \(G_{\text{head}} = kT\Delta P_{(s)}\). Derivation, with respect to the numbers of attached chains, yields to the chemical potential of a polymer chain on the surface.

\[
\frac{\mu_{P(s)} - \mu_{P(s)}}{kT} \left|_{\sigma_{P(s)}}^{\sigma_{P(s)}} \right| = NA(\sigma_{P(s)}) + \Delta P_{(s)} + \ln\sigma_{P(s)} + 1
\]  

(5.13)

After deviation of eq. 5.13 with respect to the number of chains in solution we obtain the following equation, which is valid in a dilute regime, where no micelle formation is expected.

\[
\frac{\mu_{P(l)} - \mu_{P(l)}}{kT} = \frac{N\nu\phi_{P(l)}}{l^3} + \ln\phi_{P(l)} + 1 + \zeta_{P(l)}
\]  

(5.14)
The first term is derived from the excluded volume interactions between the segments. The next two terms refer to a translational entropic contribution whereas the last one is a dimensionless term $\zeta_{P(l)}$ that gives a contribution to the chemical potential from the interactions of the ionic headgroup with the environment. $N$ is again the polymerization index and $l$ is the Kuhn length. $\Phi_{P(l)}$ is the volume fraction of the polymer in solution.

Inserting eq. 5.9, 5.10, 5.13 and eq. 5.14 in eq. 5.8 one obtains after several transformation a solution for the standard Gibbs energy

$$\frac{\Delta G^0_R}{RT} = - \frac{N\nu P(l)}{l^3} \ln \phi_P(l) + \ln \phi_I(l) + \frac{\sigma_P(s)}{NA} + \Delta P(s) +$$

$$\Delta P(s) + \ln \sigma_I(l) - \sigma_I(l) - \zeta_P(s) + \zeta_I(l)$$

The equilibrium constant is related to the standard Gibbs energy in the following way

$$K = \exp \left( \frac{\Delta G^0_R}{RT} \right)$$

Before inserting eq. 5.15 in eq. 5.16, the parameters in eq. 5.15 have to be transformed into parameters that we use in our ion-exchange experiments, namely $\Gamma_a$ and $a$.

### 5.4.1 Transformation of the parameter into system parameter $a$ and $\Gamma_a$

In general, the $a$ and $\Gamma_a$ values were previously described (Chapter 2). We would like to review briefly to what these two parameters are referring to. The $a$-value is related to the number of molecules/ions in solution per surface area through, whereas the $\Gamma_a$-value refers to the number of molecules/ions on the surface, as follows

$$\Gamma_a = \frac{n_C(s)}{F \cdot m_{Mica}}$$

$$a = \frac{n_C(l)}{F \cdot m_{Mica}}$$
where the factor $F$ in the above two equations refers to the accessible surface area per gram, $n_{C(l)}$ is the number of molecules in solution for either polymer ($C = P$), or ion ($C = I$), and $n_{C(S)}$ is the number of molecules on the surface for either polymer ($C = P$), or ion ($C = I$). In the denominator, $m_{Mica}$ refers to the mass of added mica to the solution. With these two equations, we are now able to transform all the relevant parameters in eq. 5.15:

\[
\phi_{P(l)} = \frac{N n_{P(l)} V_{I(l)}}{V_{tot}} = \frac{(N(n_{P(l)} V_{I(l)}))/F}{V_{tot}/F} = \frac{N[a - \Gamma_a]}{V_{tot}/F} V_{I(l)} \tag{5.19}
\]

\[
\sigma_{P(s)} = \frac{l^2}{N_L \Gamma_P} \tag{5.20}
\]

\[
\phi_{I(l)} = \frac{n_{I(l)} V_{I(l)}}{V_{tot}} = \frac{(n_{I(l)} V_{I(l)})/F}{V_{tot}/F} = \frac{\Gamma_a}{(V_{tot}/F)^{1/2}} V_{I(l)} \tag{5.21}
\]

\[
\sigma_{I(s)} = \frac{l^2}{N_L (S - \Gamma_a)} \tag{5.22}
\]

as functions which contain only measurable parameters. In eq. 5.19-5.22, $N_L$ is Avogadro’s constant and $n_{P(l)}$ and $n_{I(l)}$ are the number of polymers and ions in solution. Furthermore, $S$ is the total coverage of the surface measured in $\mu$mol/m$^2$. As mentioned before, we regard the volume of one monomeric unit as equivalent to the volume occupied by a small ion. From this assumption, we are able to derive the volume occupied by one polymer chain, which is equivalent to $N V_{I(l)}$. Furthermore, the contribution $\zeta$ for the polymer endgroup and the ions are on the one hand very small ($\sim 0$) and cancel each other, so that they do not affect the Gibbs free energy. Also, the two $\Delta$ parameters cancel due to the assumption, that the binding energy with the surface of the ammonium endgroup is nearly the same as for the small ions.

Inserting eq. 5.19-5.22 in eq. 5.15, and further eq. 5.15 in eq. 5.16 this results into the following expression for the ion exchange constant $K_{scf}$ for the equilibrium ion exchange reaction:
\[
K_{scf} = \frac{K}{N} \cdot \exp \left[ NA (\sigma_{p(s)}) - \frac{Nv\phi_p(l)}{l^3} \right]
\]  
(5.23)

with,

\[
K = \frac{\Gamma_a^2}{[S - \Gamma_a] [a - \Gamma_a]}
\]  
(5.24)

Eq. 5.24 is the equation for ion-exchange without entropic effects. The exponent in eq. 5.23 can be easily calculated using the following two relationships:

\[
\mu (z = h) = kT \cdot \frac{\nu}{l^3} (\phi_p(l)) \bigg|_{z = h}
\]  
(5.25)

\[
\mu (z) = kT \cdot \left( A (\sigma_{p(s)}) - \frac{1}{8} \left( \frac{\pi z}{Nl} \right)^2 \right)
\]  
(5.26)

where \( \nu \) in eq. 5.25 is the excluded volume parameter, and \( z \) is the distance perpendicular to the surface. Equating eq. 5.25 and eq. 5.26 with \( z = h \) results:

\[
\left[ NA (\sigma_{p(s)}) - \frac{Nv\phi_p(l)}{l^3} \right] = \frac{1}{8N} \left( \frac{\pi h}{l} \right)^2 \bigg|_{z = h}
\]  
(5.27)

Inserting eq. 5.27 in eq. 5.23 together with the result obtained by Ligoure and Leibler shows that the equilibrium brush height \( h \) is equivalent to

\[
h = N \left[ \left( \frac{12}{\pi^2} \right) \sigma_{p(s)} \nu \right]^{1/3}
\]  
(5.28)

and this results to the following equation for the equilibrium constant. Using \( l = 3.5 \ \text{Å} \), which is equivalent to the length of a monomer unit in poly(ethylene oxide), we obtain the following equation:

\[
K_{scf} = \frac{H}{N} \cdot \exp \left[ \frac{N}{8} \left[ 12\pi l^2 (1 - 2\chi) N_L \Gamma_a \right]^{2/3} \right]
\]  
(5.29)

where \( \chi \) is the Flory parameter for polymer solvent mixtures\[21].

The analytical self-consistent field theory describes the equilibrium constant \( K \) with an additional exponential factor describing the entropy effect of the tail part. The entropy of
the chain stretching should therefore scale with a power law of 0.66 in the adsorbed amount.

Assuming, that the equilibrium constant $K$, as derived by experiment, can be divided into an headgroup part and a tail part, we can now compare our experimental results to theoretical methods. The analytical SCF method provide the following results, summarized in Table 5.2.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$K$</th>
<th>$\Delta S_{\text{tail}}/k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>0.019</td>
<td>-3.96</td>
</tr>
<tr>
<td>117</td>
<td>9.74 \cdot 10^{-4}</td>
<td>-6.93</td>
</tr>
<tr>
<td>234</td>
<td>5.27 \cdot 10^{-5}</td>
<td>-9.85</td>
</tr>
</tbody>
</table>

The entropy penalty due to the grafting process can be determined by using experimental data in the strong stretching regime.

5.5 A look at other theories

Alternative theoretical models are available to describe the end-grafted polymers at interfaces in the stretched brush regime. Alexander and de Gennes\cite{18} have developed a scaling description by which polymers are supposed to stretch away from the surface. The polymer density, as a function of the distance from the surface, is believed to be uniform, whereas the monomer density profile of the polymer chains described by the SCF theory is parabolic. The changes that occur are changes in the exponent of the power law for the stretching free energy of the brush. Using the Alexander-de Gennes ansatz for polymer at interfaces, where only weak interactions of the polymer are
allowed with the surface, we derive the following equation for the equilibrium constant penalty due to grafting, as:

\[
\frac{\Delta S_{\text{scaling}}}{k} = -N \left( \frac{\Gamma_a}{S_{\text{unicell}}} \right)^{\frac{5}{6}}
\]

(5.30)

where \( S_{\text{unicell}} \) is the surface area of a unit cell of mica. Murat and Grest show some interesting molecular dynamics simulation on polymers grafted to a flat surface\textsuperscript{[19]}. They performed dynamics simulation on polybeads by varying the polymerization index, the grafting density, and the temperature. As one of their results, the root mean square end-to-end distance of the chains was computed. We relate those values to the unperturbed dimensions of a polymer coil and get the following equation for the entropy change due to their dynamic simulation\textsuperscript{[24]}

\[
\frac{\Delta S_{\text{MD}}}{k} = \frac{3}{2} \left[ \frac{\langle r^2 \rangle}{\langle r^2 \rangle_{\text{free}}} - 1 \right]
\]

(5.31)

In eq. 5.31, \( \langle r^2 \rangle \) refers to the mean square radius of gyration of the chains on the surface and \( \langle r^2 \rangle_{\text{free}} \) stands for the unperturbed radius of gyration of a polymer in solution. The quotient in eq. 5.31 can be expressed by a power law for the dense brush regime. The coefficients of the power law are derived by fitting the results of Murat and Grest to it. One obtains the following equation

\[
\frac{\langle r^2 \rangle}{\langle r^2 \rangle_{\text{free}}} = 0.83 \left[ \frac{3}{x^2 \Gamma_a} \right]^{\frac{1}{3}}
\]

(5.32)

With eq. 5.32 and eq. 5.31, it is possible to calculate the entropy difference between the tethered chains and the chains on the surface. Because of lack of the chains, the results for \( x = 1 \) are equal to zero. As a result, the corresponding entropy penalty of each method is listed in Table 5.4.
Table 5.4
Experimental and theoretical results of the entropy change in units of the Boltzmann constant $k$.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta S_{\text{tail}}/k$</th>
<th>\textbf{exp.}</th>
<th>\textbf{anal. SCF}</th>
<th>\textbf{Alexander/De Gennes$^{[18]}$}</th>
<th>\textbf{Murat &amp; Grest$^{[19]}$}</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>-5.57</td>
<td>-3.78</td>
<td>-7.23</td>
<td>-4.75</td>
<td></td>
</tr>
<tr>
<td>117</td>
<td>-7.34</td>
<td>-4.66</td>
<td>-10.10</td>
<td>-6.37</td>
<td></td>
</tr>
<tr>
<td>234</td>
<td>-8.73</td>
<td>-5.33</td>
<td>-11.34</td>
<td>-7.34</td>
<td></td>
</tr>
</tbody>
</table>

For comparison, we have plotted the values of $\Delta S$ vs. $\ln K$ in Figure 5.4.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.4}
\caption{Comparison of the entropy change of the chains on the surface with theoretical treatments of the brush entropy as derived by self-consistent mean-field methods, scaling description and molecular dynamics simulation.}
\end{figure}
Using the Alexander-de Gennes, this Ansatz over-estimates the entropy change on the surface relative to the numbers obtained by experiment. This over-estimation results from the assumption of strongly stretched chains. According to Alexander, the polymeric chain is attached with the head group to the surface, stretching away from it, and it can be confined in a tube or a cylinder perpendicular to the surface. The length of the tube is equivalent to the brush height and the area on the bottom refers to the average grafting area of the polymer head group. Therefore, a strong stretching and a large decrease in entropy is estimated for this regime. The SCF-ansatz reveals some lower values for the entropy change. This discrepancy, as well as for the other theories may not only result from a pure assignment of the polymerization index and the monomer length. Many experimentalists equate the polymerization index to the one used in theories. The model behind those theories is sometimes not consistent with the experimental system, because the assumptions of flexibility of the chain are not fulfilled. Changes in the polymerization index would modify the entropy change.

Further, another error is the over-estimation of the mean-field ansatz for the repulsive and the attractive terms as discussed by de Gennes\textsuperscript{[20]}. All theories describe the entropy change in the form of a power law. The change in the exponent causes a change in entropy. As can be seen, the power law of the self-consistent mean field methods under-estimate the change in entropy whereas the strong-stretching ansatz of Alexander-de Gennes over-estimates this behavior. Nevertheless, we can conclude that the theories developed are not in contradiction by an order of magnitude relative to the experimental system. Using a general scaling ansatz for the power law dependence of the experiment on the entropy in the following form

\[
\frac{\Delta S}{k} = -N \left( \frac{\Gamma a}{S} \right)^\lambda
\]

and fitting this equation to our experimental system, we obtain a value of \( \lambda = 0.94 \). This value is used for the strong stretching approach.
5.6 Description of polymer brush formation with analytical SCF tools.

We have derived an expression for the adsorption isotherm behavior of cation-terminated polymers, using the analytical self-consistent field approach. This allows a wide variety of parameters to be adjusted such as the solvent quality or the polymerization index. In the following section, we will give a general description of the dependence on these parameters of the adsorption behavior and polymer brush formation via ion exchange.

5.6.2 K-dependence

The equilibrium constant $K$ is a system variable and constant under fixed conditions. It can be influenced by temperature or pressure changes, and, as a result, the equilibrium is pushed in one of the two directions. Changes in temperature always accomplishes changes in solvent quality of a polymer solution. This means that the molecular size of the dissolved polymer changes with increasing temperature. Therefore, changes in temperature are taken into account by changing the solvent quality. This effect is used the other way round in the simulations of Murat and Grest, in which they simulated the solvent quality by changing the temperature of the molecular dynamics simulation. A change in temperature causes not only a change in the size of the polymer but also in the Gibbs energy of the polymer ion exchange reaction. The relationship between those influences on the adsorbed amount are manifold and difficult to separate and therefore difficult to describe. On the other side, we can calculate the isotherms with varying the equilibrium constant. The equilibrium constant is a result of external changes on the system and implies all system parameter. In Figure 5.5, we have shown the change of adsorbed amount at various equilibrium constants $K$.  

Figure 5.5 Calculated adsorption isotherms using SCMF methods at varying equilibrium constants. The change of the equilibrium constant is due to many changes of system parameters and is described in the text.

5.6.3 Solvent quality

As it can be seen in eq. 5.29, the amount of polymer adsorbed on the surface is also dependent on the solvent quality. Changes in solvent quality modifies the interaction energy between solvent molecules and polymer chain segments. As a result, the chain dimensions as measured by the radius of gyration will change. The radius of gyration $R_g$ is dependent on the polymer chain length according to

$$R_g = ax^b$$

(5.34)

where, $a$ and $b$ are constants, and $x$ is the polymerization index. Changes in the interaction energy between solute and solvent also arise from temperature changes. Therefore, by altering the temperature, the coil dimensions may change. In the following plot, we show the change in amount of polymer adsorbed for different Flory interaction parameters $\chi$ (see also eq. 5.29) (Figure 5.6).
Figure 5.6 Calculated adsorption isotherm at varying solvent quality values as determined by the Flory interaction parameter $\chi$ (from eq. 5.29).

5.6.4 Competitive ion-exchange adsorption by adding external inorganic salt

As mentioned by several authors, it is very difficult to measure the radius of gyration of PEG by spectroscopy methods. PEO contains two theta temperatures near 0 °C and 100 °C in aqueous solution depending on the molecular weight (see ref. 14 and refs. in there). In between these two point, the PEG coils are extremely swollen and water serves as a good solvent in the absence of salt. The addition of salt to a solution of PEO in pure water raises the theta temperature and lowers consulate temperature (LCT), depending on the concentration and type of salt. The addition of salt has two opposing effects that must be separated. On one hand, due to the presence of ions with a certain ionic strength, the size of the polymer shrinks and the free space on the surface for further polymers increases. On the other hand, a certain concentration of inorganic ions in solution will drive the equilibrium back in the direction of the starting product. We separate those two opposing effects and assume at first that the polymer size is not influenced by the presence of ions. Therefore, only the externally added amount of salt will causes a change in the amount of polymer adsorbed. Theoretically, we can determine the volume
fraction of ions in solution according to

\[
\phi_{I(l)} = \frac{(n_{I(l)} + cV_{tot})V_{I(l)}}{V_{tot}} = \frac{(a_{I(l)} + c\frac{V_{tot}}{Fm})V_{I(l)}}{V_{tot}/(Fm)} = \frac{\Gamma_a + a\frac{c_{I(l)}}{c_{P(l)}}}{(V_{tot}/F)}V_{I(l)} \tag{5.35}
\]

where the c's are the initial concentrations in the solution. We have to modify eq. 5.24 accordingly, and get

\[
H = \frac{\Gamma_a (\Gamma_a + a\frac{c_{I(l)}}{c_{P(l)}})}{[S - \Gamma_a][a - \Gamma_a]} = \frac{\Gamma_a (\Gamma_a + a\kappa)}{[S - \Gamma_a][a - \Gamma_a]} \tag{5.36}
\]

where \( \kappa \) is the concentration ratio between cations from salt and polymer in solution. In this equation, we imply that there is no other type of salt added to the solution. Another type of salt will cause a change in the interaction parameters, and the assumption we made initially on the surface interactions cannot be hold. The adsorption isotherms for different ratios can be seen in Figure 5.7.

**Figure 5.7** Adsorption isotherms of \( x = 117 \) at various ratios of \( x = 117 \) to LiBr added to the solution.
With increasing amount of external salt in solution, less polymer adsorbs on the surface. Experiments using cation-terminated PEG with different amounts of PEG show indeed such a behavior (see Chapter 6).

5.7 Conclusions

Ion exchange adsorption of cation-terminated polymers from solution offers a sensitive method to study the behavior of polymer chains on the surface. If the surface coverage increases beyond the threshold of the cross-over regime, the chains have to stretch away from the surface and form a dense brush. The stretching causes a penalty in entropy. Theoretical methods have been developed in the past 30 years to calculate the behavior of those grafted chains and to determine the entropy changes. The accuracy and validity of those methods has to be proven with an experimental model system. The comparison to these theoretical methods shows remarkably fair agreement within an interval of $2k_B$ of the experimental system. The entropy change as derived by Murat and Grest closely resembles the experimental results. As a result, in the strong stretching regime, it is possible to apply theoretical methods to derive entropy changes of the system. Attention has to be paid that the experimental data are indeed in the overlapping and stretching regime. The ion exchange process with cation-terminated polymers holds considerable promise in helping to understand the complex behavior of adsorbed polymer layers. It tests the predictions of current models for the chemical potential of the end-grafted chains on the surface.

We derived an expression to estimate the equilibrium constant for ion exchange reactions with polymers attached to flat surfaces with exchangeable ions on it. It is shown elsewhere that this reaction is always in equilibrium and the adsorption isotherms are equilibrium ion exchange isotherms. Using the analytical SCF methods developed by Milner, Witten and Cates and further by Ligoure and Leibler, we were able to derive expressions for the chemical potential of the ions on the surface and in solution. We quantify the entropy for the ion exchange reaction with respect to the chain length, if we
fit our equations to the appropriate ion exchange isotherm. Knowing, or estimating, different system parameters, such as the equilibrium constant, or the excluded volume parameter, we are able to plot adsorption isotherms that indicate the way in which a particular system behaves under these special conditions. Therefore many systems that deal with ion-exchange on ionic surfaces can be described with our equations, if the polymers bear a charge at their end and are in equilibrium with the solution. The applicability of our equations can be proven with further experiments.
References


6. Factors Determining the Brush Formation

6.1 Introduction

In Chapter 2, we have shown that cation-terminated poly(ethylene glycol) chains adsorb from the aqueous solutions on mica surfaces by the ion-exchange with inorganic ions on the mica surfaces. The adsorption behavior of these cation-terminated polymers differs significantly from that of small organic and inorganic cations. The small cations can completely exchange the inorganic ions initially present on the mica surface; they exhibited adsorption isotherms with "plateaus" corresponding to complete exchange. In contrast, although the cation-terminated polymers also exhibit isotherms with plateaus, the plateaus were well below the ion exchange capacity of the surface. The plateaus are found to have lower values when the polymer chains are larger, and this was attributed to the interactions between the adsorbed chains on the surface. It was suggested that these effects could in fact be used as a sensitive tool to study the interactions between chains. If this hypothesis concerning the isotherms is correct, the isotherms should be strongly influenced by the quality of the solvent surrounding the chains, as this will influence the dimensions of the polymer "coil" and the polymer-solvent versus polymer-polymer interaction. In the present study, the solvent quality has been varied by a) using ethanol/water and glycol/water mixtures as the solvent in the polymer solution, and b) adding lithium bromide to the polymer solution. The effect of temperature change has also been examined.
6.2 Results

6.2.1 Mixtures of ethanol and water

We have investigated the changes in the adsorbed amount of poly(ethylene glycol) grafted to a mica surface for various solvent mixtures of water and ethanol. A change in the type of solvent or a change in the relative amounts of two solvents in a mixture causes a change in solvent quality parameter for the polymer-solvent interactions. In order to get a better understanding of those effects, we have determined the ion-exchange adsorption isotherm at various ratios of water/ethanol mixtures for different polymer chain lengths of cation-terminated PEG.
Figure 6.1 Ion-exchange adsorption isotherms as determined by TGA for poly(ethylene oxide) for various solvent mixtures of ethanol and water as indicated in the Figures. a) x=1, b) x=47, c) x=117. The dashed lines are guides to the eyes.
Also, we have made the comparison to a single monomeric unit of ethylene glycol terminated by a trimethylammonium- and a methoxy-end group (see Chapter 2). In the following, we show the behavior of the adsorption isotherms for $x=1$, $x=47$, $x=117$ (Figure 6.1a-c).

In the case of $x=234$, the adsorption isotherm closely parallels the shape of the other polymers with a lowered plateau value. The $a$-value and the $\Gamma_a$-value are given in $\mu$mol/m$^2$, where the $a$-value determines the number of polymer molecules with respect to the accessible area or with respect to the number of exchangeable sites on the surface. The $\Gamma_a$-value determines the number of polymer molecules grafted to the surface with respect to the accessible area on the surface. The number of exchangeable sites on the surface can be determined by multiplication with the characteristic ratio of unit-surface-area per ions-per-unit-surface area. This ratio can be determined from the crystal structure. The changes in the plateau values for the ion-exchange isotherm at different ratios of ethanol to water are displayed in Figure 6.2.

**Figure 6.2** Ion-exchange plateau values as a function of the mass ratio of water to ethanol. Also indicated are the values for $x=234$ not displayed separately in Figure 6.1. The polymerization index is indicated in the legend. The dashed line are just guides for the eyes.
The ion-exchange behavior of the head group, $x=1$, is not dramatically influenced by the change from one solvent to another solvent. The plateau values normally range between 2.5 and 3.4 μmol/m$^2$. With increasing content of ethanol in the ethanol-water mixture, the plateau value drops for the case of $x=1$. For all solvent mixtures, the plateau values decrease with increasing chain length. At 50 w/w of ethanol, the plateau values as determined by visual construction experience a minimum, whereas high ion-exchange adsorption values are found for the pure solvent case. Interestingly, similar effects with respect to such a minimum at 50 w/w, can be found for the heat of dilution of PEG at various ratios of ethanol to water$^{[1]}$. The apparent molar heat capacity of low molecular weight PEG also shows a substantial minimum at ca. 50 w/w compared to that in ethanol or water.

### 6.2.2 Water-Glycol mixtures

The purpose of this part of the investigation is to study the polymer brush formation in a solvent mixture of a good solvent for poly(ethylene glycol) and a non-solvent. With increasing amount of non-solvent, in our work ethylene glycol, the swelling behaviour should be reduced and the size of the chains should be decreased. The ion-exchange adsorption isotherm of different kinds of water/ethylene glycol ratios can be seen in Figure 6.3a-c for $x = 1$, $x = 47$ and $x = 117$. The data for $x = 234$ follow the same trend as those of the other two polymers.
Figure 6.3 Ion-exchange adsorption isotherms for the water/glycol mixtures. We have determined the isotherms up to a ratio of 50 w/w glycol to water because of the difficult dispersivity of the mica particles at higher ratios a) x=1, b) x=47, c) x=117.

6.2.3 Changes in temperature.

It is well known that poly(ethylene glycol) contains two consolate temperatures. These two temperatures, known as the upper consolate temperature (UCT) and lower consolate temperature (LCT), are dependent on the molecular weight of the PEG\textsuperscript{[21]}. In the molecular weight range of several thousands, PEG exhibits an UCT higher than 100°C whereas the LCT is lower than 0 °C. In between, the water is considered to be a good solvent. Neutron reflectivity\textsuperscript{[3]} studies by Cosgrove et al. indicate that even within the temperature range from 30 °C to 70 °C a change of the density profile of attached PEG chains to a flat surface can be determined. They found that a change in temperature causes a flattening of the volume fraction profile of the polymer which indicates a change in solvent quality from good to bad solvent conditions. We have determined the ion-
exchange adsorption isotherms at three different temperatures of 34, 50 and 70 °C. In the following figure, we summarize the results obtained by changing the temperature for various molecular dimensions (Figure 6.4).

![Figure 6.4](image.png)

**Figure 6.4** Ion-exchange isotherms at different temperatures for $x = 1$, $x = 47$, and $x = 117$. The amount of polymer adsorbed is plotted on a logarithmic scale vs. the amount of polymer in solution per unit area. The dashed lines are just guides for the eyes.

Changes in temperature enter in the equation of state for the free energy of the reaction by changing the entropy contribution to the total free energy. On the other side, the alteration of temperature has simultaneously two effects on the ion-exchange process, namely a change in the molecular dimensions and a change in the equilibrium constant of the ion-exchange process itself.

The delamination process of the mica sheets is not to be taken into account, because the reaction is carried out in aqueous solution and ultrasounds are used prior to performing the reaction. The temperature effect is also measured for the monomeric compound
(x=1). The entropy effects of the polymer brush formation can be derived from the ion-exchange adsorption isotherm of the polymeric compounds, as described previously.

A trend for the plateau values towards higher $\Gamma_a$-values is visible but not significant. The scatter of the experimental data points, and the resulting experimental error, as well as the analysis of the adsorbed amount of polymer by TGA exceed the differences in the plateau values for different temperatures in the plateau regime. Therefore, we give only a vague confirmation of the effects observed by Cosgrove. Despite the fact that these changes can be nicely determined with sophisticated neutron reflection methods, our method does not allow the determination of those changes.

6.2.4 Externally added lithium bromide.

According to Le Chatelier's principle, it should be possible to shift the equilibrium side of the dissolved polymer by adding a certain amount of salt to the reaction. In order to influence the equilibrium constant, we have investigated quantitatively the lowering in the plateau value with increasing amount of lithium bromide, in solution. We applied a huge excess of added lithium bromide to the solution, such that the assumption of a constant concentration of lithium bromide in solution holds. Specifically, we applied a 2, 7 and 14 fold excess of lithium bromide with respect to the molar amount of PEG in the system. The release of lithium ions from the surface that results from ion-exchange with cation-terminated PEG does not significantly change the concentration of lithium bromide in solution due to the large excess applied. The results on the adsorption and ion-exchange behavior, respectively, are shown in Figure 6.5.
Poly(ethylene glycol) dissolves in many organic solvents as well as in aqueous media. On the other hand, it is difficult to find solvents that are suitable for the study of the ion-exchange adsorption behavior on mica. At least three conditions have to be fulfilled in order to study the polymer brush formation of PEG on mica surfaces: (1) the PEG must be soluble in the solvent; (2) the mica must be dispersible; (3) the ions must be solvated. With respect to the solubility of PEG, this rather strange behavior of a polymer is due to its hydrophobic and hydrophilic parts in the chain. The ethylene unit is the hydrophobic part whereas the ether oxygen is responsible for the hydrophilic part. The solution behavior of poly(ethylene glycol) in various solvents is studied by a number of

**Figure 6.5** Ion-exchange adsorption of PEG at various LiBr/PEG ratios. a) $x = 1$ with different amount of added lithium bromide; b) $x = 47$ and c) $x = 117$. With increasing amount of lithium bromide in solution, less polymer goes on the surface.
experimental techniques and the conformational changes for this polymer are of great interest for computer simulation. The behavior of poly(ethylene glycol) in aqueous and non-aqueous solvents is summarized by Molyneux\textsuperscript{[4]}\textsuperscript{[4]}. In aqueous media, PEG exhibits an upper and a lower consulate temperature (UCT and LCT)\textsuperscript{[5]}. At substantial high molecular weights of ca. 100,000, the LCT can be found at 0 °C whereas the UCT, where the poly(ethylene glycol) phase separates from the aqueous phase, is at ca. 100 °C. In between, water dissolves PEG and is believed to be a good solvent at ambient temperatures of 34 °C in the absence of inorganic ions. The molecular dimensions of PEG can also be determined by static and dynamic light scattering methods\textsuperscript{[5]}. It turns out that the exponent for the exponential dependence of the radius of gyration on the molecular weight corresponds to the good solvent regime. These values are close to the theoretical value of 0.6, as derived by Flory\textsuperscript{[6]} and those of 0.588 as derived by renormalization group theory\textsuperscript{[7]}. Changing the solvent from water to ethanol, the solution behavior changes dramatically. Whereas, an LCT and an UCT can be found in aqueous phases, only the LCT can be determined for poly(ethylene glycol) in most organic solvents. With increasing temperature, the solution behavior becomes even better\textsuperscript{[4]}. Also, the chain conformation in solution changes. The preferred TGT (trans-gauche-trans) conformation of PEG in aqueous solution changes into a random orientation of the chain in organic solvents.

A measure of the solvent quality for different kind of solvents for PEG can be obtained by using solubility parameters. The solubility parameter \( \delta \) for ethanol is 26.0 (J/m\(^3\))\(^{1/2} \) whereas the solubility parameter for water has a value of 47.9 (J/m\(^3\))\(^{1/2} \)\textsuperscript{[8]}. Poly(ethylene glycol) itself has a solubility parameter of 19.4 (J/m\(^3\))\(^{1/2} \)\textsuperscript{[9]}. As it can be seen, the solubility parameter for ethanol is much closer to the value of PEG than the one for water. The closer the solubility parameter match, the better miscible the components should be. Nevertheless, water is believed to be a better solvent for PEG than ethanol at 34°C. We attribute this effect to the different kinds of solvation and up to now it is unknown how these changes in solvation look. Further, the swelling properties of a polymer in solution are dependent on the polymer-solvent interaction parameter. Generally, this parameter is expressed by the Flory interaction parameter \( \chi \). The shortcoming of Flory's interaction parameter is that only binary systems can be
investigated. In a multicomponent system, this theory fails, and it is difficult to judge how the isotherms will look for mixtures of two solvents based on the interaction parameter\(^9\). At first, the lower plateau values of PEG for the mixed solvent systems may be due to an increased size of the polymer chains at the surface. Other effects are the change in hydration energy of the monomeric units and the influences on the ion exchange process itself. It is difficult to separate each of those effects. We overcome this problem by determining the influence of the change in solvent quality for the head group alone. Using this approach, we include all necessary interaction in the head group analysis (see Chapter 3). As a result, changes in the adsorption isotherm are based only on the thermodynamic properties of the system. The contribution to the free energy of the ion exchange reaction can be determined qualitatively whereas a quantitative description it not visible at the moment.

The interaction energy of the solvent with the lithium ions changes upon changing the content of the solvent mixture. In our case, the Gibbs energy for the transfer of one lithium ion from aqueous media into ethanol requires 11.1 kJ/mol \(^{10}\). Therefore, it is less favorable for the lithium ions to be solvated by ethanol molecules than by the water molecules. As a consequence, the equilibrium will be shifted back and the adsorption isotherms lowered. As the influence on the head group of the polymers is determined by performing the adsorption reaction with \(x = 1\), the changes in the thermodynamics of the head group can be separated from the thermodynamics of the tail part. Calculating the entropy change in units of the Boltzmann constant \(k\), as derived in the Appendix I, we are able to determine the effects of the chain length on the polymer brush formation. In Figure 6.6, we plot the entropy penalty in units of \(k\) against the mass ratio of water to ethanol.

As it can be seen by the changes in the plateau values with varying ratios of ethanol/water, the entropy goes through a minimum at ca 50 w/w of ethanol to water. The lines in Figure 6.6 are just to guide the eyes. The experimental data follow a parabolic function.

In the case of ethylene glycol, the solubility parameter for ethylene glycol is 29.9 (J/m\(^3\))\(^{1/2}\), a value which is not very different from that of ethanol, with respect to the
difference to water. At first glance, one expects that PEG should be soluble also in ethylene glycol. On the other hand, ethylene glycol is a non-solvent for PEG at any temperature. The main disadvantage of the water/glycol system are swelling and delamination problems of the mica itself. At ambient temperatures of 34 °C, the swelling properties of ethylene glycol for the mica we used are very low\textsuperscript{[12]}. Therefore, a pre-swelling of the mica material in aqueous solutions was necessary to get the layers delaminated. After incubation of the mica powder with several drops of water, the solution mixture was added to the mica powder.

![Figure 6.6 Entropy penalty of PEG with increasing w/w of ethanol in water for $x = 47$, $x = 117$, and $x = 234$. The dashed lines are just guides for the eyes.](image)

Even with this sequential delamination procedure, there is no clear evidence that the same surface area is accessible in mixtures of water and glycol as in water. Consequently, we just discuss the effect of water/glycol mixtures qualitatively. In the
simplest case, \( x=1 \), the ion-exchange adsorption plateau values decrease with increasing the concentration of ethylene glycol in solution. Due to delamination problems, we have not investigated the polymer brush formation behavior at ratios of more than 50 w/w of ethylene glycol. The decrease of the plateau values can be explained by applying the same arguments as in the water-ethanol case. Ion-exchange is not only determined by the free energy difference of the adsorbed compounds on the surface. It depends also on the solvation free energy of the compound in solution, and the changes of the plateau values can also be a result of the lowered solvation energy of lithium ions in solution. The hydration and solvation of small inorganic ions is therefore reduced in such solvent mixtures\(^{11}\).

This effect inevitably reduces the maximum ion-exchanged amount of \( x = 1 \) on the surface. The change in the plateau values of the higher molecular weight compounds \( x = 47 \) and \( x = 117 \) and also \( x = 234 \) is therefore mainly influenced by two hardly separable opposing effects. The change in solvent quality should, on one hand, influence the radius of gyration as well as the hydrodynamic radius. On the other hand, the interactions with the headgroup have changed. The surrounding poly(ethylene glycol) has the ability to complex inorganic ions in solution. The lower the solvent quality becomes, the more the formation of poly(ethylene glycol) clusters is favored. This complication of the system even in ethylene glycol-water mixtures leads us to the conclusion that it is very difficult to get a reasonable explanation of the experimental results for these systems.

In the case of ethylene glycol/water mixtures, we have applied the same procedure to determine the entropy penalty as in the ethanol-water case. The results can be seen in the Figure 6.7 up to a mass ratio of 50 w/w. The entropy change is still negative for those cases and decreases with increasing content of ethylene glycol.
In the case of added lithium bromide, we have tried to evaluate the mass action effect by the following methodology. The equilibrium constant does not change for a given reaction, by changing the concentration of a certain component in the equilibrium. Therefore, this constant is believed to be constant under the conditions where we add some further salt to the solution. The equilibrium constant, K, is determined as given in the Appendix I. The same equilibrium constant is used to derive theoretical plots, in which we include the effect of change in concentration of externally added lithium (see Appendix II). Figure 6.8, we have plotted the theoretical mass action coefficient against the experimental values. As a result, the theoretical mass action isotherms are always lower than the measured adsorption isotherms. Consequently, there must be an additional driving force that shifts the equilibrium in the direction of grafted chains. This can be a result of some combined effects. (1) The change in the chain dimensions due to changing the solvent quality upon adding salt to the solution; (2) changes in the surface potential;
(3) agglomeration effects caused by complexes of lithium and PEG.

![Graph showing masaction effect against experimental data for x = 1, x = 47, and x = 117. The trend for x = 234 is the same as those for the lower molecular weight data. The plateau values of the isotherms decrease with increasing a-value. We expect that the solvent quality is reduced due to adding some amount of salt to the solution and therefore the plateau values should increase.](image-url)
6.4 Conclusions

We have studied the ion-exchange behavior of cation-terminated PEG on mica surface in different solvent media, at various temperatures and at different ratios of lithium bromide to PEG in solution. Change of the ethanol to water ratio results into a change of the adsorption isotherm. As a striking result, the plateau values of those isotherms go through a minimum while increasing the content of ethanol in the aqueous solution. Different hydration modes can be made responsible for those effects. Also glycol/water mixtures, where water is believed to be a good solvent for PEG and glycol is believed to be a non-solvent, were studied. The complex hydration and solvation effects are summarized as resulting isotherm. It was found that the plateau values constantly decrease with increasing content of glycol. We did not go beyond the threshold of 50 w/w of ethylene glycol to water, because of the poor dispersivity of muscovite mica, as prepared, with increasing amount of glycol. We were not able to determine a significant change in the adsorption isotherm and the polymer brush formation behavior upon changing the temperature.

The influence of added lithium bromide was also investigated. We found, that the isotherms, as calculated only from the mass action effect, always resulted in isotherms much lower than the experimental isotherms. Changes in solvent quality and complexation are responsible for this decrease.
For the polymer, the changes of the chemical potential for this reaction can be written as

\[
\frac{\Delta \mu_{\text{polymer}}}{kT} = \frac{\Delta \mu_{\text{head}}}{kT} + \frac{\Delta \mu_{\text{tail}}}{kT}
\]  

(6.1)

The change in the chemical potential for this reaction can be divided into two parts. One part is the change due to bringing the head group from solution to the surface and the other part results from changes of the tail of the polymer due to changes in configurational space of the confined polymer at the interface. The first term, mainly, has an enthalpic function. While the polymer is adsorbed, the Flory-interaction parameter does not change at a first glance and therefore, the changes in the enthalpic part of the last term cancel out. What remains is the entropic part. The first term can be determined by performing the ion-exchange reaction only with the headgroup of the polymer. This molecule can be identified as \( x=1 \). The change in the chemical potential of the complete system can also be determined. Therefore, the tail-free energy can be calculated as follows:

\[
\frac{\Delta \mu_{\text{polymer}}}{kT} - \frac{\Delta \mu_{\text{head}}}{kT} = \ln \left( \frac{K_{\text{head}}}{K_{\text{polymer}}} \right) - \frac{\Delta \mu_{\text{tail}}}{kT} = \left( \frac{\Delta S_{\text{tail}}}{k} \right)
\]  

(6.2)

The difference on the right side of eq. 6.2 can be determined experimentally. Therefore, changes in entropy for the tail part of the polymer can be calculated as a function of the chain length. For the calculation of equilibrium constants, we perform a fit with the following equation, that was derived in a previous paper[13]

\[
K = \frac{\Gamma_a^2}{[S - \Gamma_a] [a - \Gamma_a]}
\]  

(6.3)

where, \( S \) is the maximum possible exchange capacity with the system, \( a \) is the amount of
polymer in solution per unit area accessible surface, and $\Gamma_a$ is the amount of polymer on the surface per unit surface area. Usually, the unit of these values is $\mu$mol/m$^2$. Fitting eq. 6.3 to the experimental data points, using a nonlinear least-square Levenberg-Marquardt algorithm, we obtain the chemical constant $K$ and for maximum exchange capacity $S$. Note that the maximum exchange capacity $S$ is a constant and does only change with the type of surface used. Inserting the equilibrium constants $K$ in eq. 6.2, we derive chain-length-dependent entropy changes for polymer adsorption.

6.6 APPENDIX II

The equation for the equilibrium constant changes upon adding a certain amount of salt externally to the solution. The quantity of the lithium ions in solution is the only quantity that changes upon adding some lithium bromide. Therefore we go from $\Gamma_a$ to $\Gamma_a + a*r$, where $a$ is the $a$-value and $r$ is the $a$-ratio or molar ratio of the lithium bromide to cationic-modified PEG in solution. The equation for the equilibrium constant changes also according to the following equation

$$K = \frac{\Gamma_a (\Gamma_a + ar)}{[S - \Gamma_a] [a - \Gamma_a]}. \Gamma_a \ll ar$$

(6.4)

$$K = \frac{\Gamma_a ar}{[S - \Gamma_a] [a - \Gamma_a]}.$$ 

(6.5)

By solving this equation, using the Levenberg-Marquardt method, we can calculate $\Gamma_a$ as a function of $a$. These plots represent the pure mass action effect on the adsorption isotherm for externally added salt.
References


7. Experimental Part

7.1 Muscovite Mica Analysis

*Polymer characterization:*
Melting points were determined with a Mettler TC11 machine at a heating rate of 10 °C/min. Molecular weight distributions were obtained by *matrix-assisted laser desorption ionization time-of-flight mass spectrometry* (MALDI-TOF MS) (Bruker REFLEX mass spectrometer) with detection in the linear mode (matrix: 0.1 M α-cyano-4-hydroxycinnamic acid (CCA) in a solvent of two parts by weight of 0.1% trifluoroacetic acid in water and one part by weight of acetonitrile). Number-average molecular weights were measured using *vapor-phase osmometry* (Corona Wescan 32A) at 50 °C with saccharose (puriss.) as reference substance (average of 3 measurements).

*X-ray diffraction:*
A suspension of mica (ca. 50 mg in 2 ml ethanol) was dropped onto the rough side of a glass slide and dried in the air. This procedure was repeated until a thin mica film covered the entire glass slide. All the samples were kept for 2 h at 40 °C and 100 mbar prior to use as a sample for X-ray diffraction. X-ray diffraction patterns were obtained for oriented film samples using a Philips diffractometer with CuKα1 and CuKα2 radiation of a ratio of 1:1.

*TGA:*
The amount of polymer bound to the surface was analysed using Perkin-Elmer TGA 7. The weight loss was determined by tangential baseline correction.

*ICP:*
The amount of lithium ion released by the adsorption was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Plasmaquant 110, Carl Zeiss Jena, Jena, Germany).
Conductivity:
The rate of adsorption was determined by experiments in a conductivity cell (Orion 99-01-03, C=0.1 cm⁻¹).

7.2 Materials and Synthesis

Synthesis of cationic PEO
The polymers α-methyl-ω-bromo-poly(oxyethylene) (2) and [α-methyl-ω-trimethylammonium-poly(oxyethylene)]bromide (3) were prepared following Bückmann, Morr, and Johansson[1]. Polyethylene glycol 2000 monomethyl ether, and polyethylene glycol 5000 monomethyl ether (Fluka, Buchs, Switzerland) were used as supplied. Solvents were dried prior to use with 4Å molecular sieves. Overall yields were in the range of 70-80%.

α-methyl-ω-bromo-poly(oxyethylene) (2)
¹H-NMR (TMS, DMSO), in ppm: 3.28 (s, 3H, H₃C-O-C), 3.38-3.62 (m, O-CH₂-CH₂-O). mp. 54 °C.

[α-methyl-ω-trimethylammonium-poly(oxyethylene)]bromide (3)
¹H-NMR (TMS, DMSO), in ppm: 3.13 (s, 9H, (CH₃)₃N⁺-), 3.28 (s, 3H, H₃C-O-C), 3.38-3.62 (m, O-CH₂-CH₂-O-). mp. 61°C.

Synthesis of 2-methoxyethyl-trimethylammonium bromide
2-Bromoethylmethylether (Aldrich Chemie, Buchs, Switzerland) (1.0 g, 7.2 mmol) was added to a solution of trimethylamine (24 ml, 4.2 M in ethanol) and the slightly brown solution stirred for 24 hours at room temperature. After cooling, evaporation of the solvent, addition of fresh ethanol (50 ml), and treatment of the residue with carbon black (ca. 0.2 g) at 50 °C, the product was precipitated at 4 °C and recrystallized two times from ethanol. The yields were typically in the range of 70-85%.
¹H-NMR (TMS, DMSO), in ppm: 3.20 (s, 9H, (CH₃)₃N⁺-), 3.32 (s, 3H, H₃C-O-C), 3.60 (t, 2H, C-O-CH₂), 3.76 (t, 2H, -CH₂-N⁺). mp. 155 °C.
Mica:

Chemicals:
Muscovite mica was supplied by Isola (Breitenbach). We refer to this mica as mica A. The alkylammonium salts of the formula \((\text{CH}_3)_3\text{N}^+(\text{CH}_2)_n\text{CH}_3, n = 4, 6, 8, 10, 12, 14, 16, 18\), were obtained from Fluka, Buchs (Switzerland). For adsorption experiments, aqueous solutions (0.25 mmol/kg) were prepared using 100-500 mg mica and 100-500 g solution. The ammonium derivatives were synthesized preparing a 0.1 M solution of the corresponding amine in ethanol followed by addition of hydrochloric acid.

Synthesis and characterization of delaminated mica:
Mica was delaminated with lithium nitrate/water mixtures, as described previously. The specific surface area (101 m\(^2\)/g) and the ion exchange capacity (382 µmol/g) were determined as described previously with methylene blue adsorption and N-dodecylpyridinium adsorption, respectively\(^2\). The specific surface area of the starting non-delaminated mica was 3-4 m\(^2\)/g.

7.3 Adsorption Experiments

Polymer:

Adsorption
The ion exchange experiments were carried out in freshly cleaned glassware, which was first rinsed with chromium sulfuric acid and then washed for several hours with water; this glassware was reused for further adsorption experiments by boiling with 3D-water for one hour. The specific ionic conductivity of 3D-water (Millipore Ultrapure) in such purified glassware was less than 0.5 µS/cm. Plasticware made of polypropylene or polyethylene was found to be unsatisfactory as it gave irreproducible results.

The substance was dissolved in 3D-water to a concentration of roughly 0.8 mM. Typically 50 mg mica were used and the desired amount of cationic-PEO solution was
added. After stirring for 6 hours at 33 °C, the mixture was centrifuged for 15 min (4000 rpm) and the supernatant solution removed and filtered through a 0.2 μm PP or PTFE filter for analysis. The solids were washed an additional 4 times with 50 ml 3D-water whereafter the conductivity of the supernatant remained constant in the range of 1 μS/cm. The solids were then dried for several hours at 40 °C under vacuum (ca. 0.01 mbar). The amount of polymer adsorbed was determined by thermogravimetric analysis (TGA) (Perkin-Elmer TGA 7). The samples for TGA were heated to 110 °C and left at this temperature for 15 min to remove adsorbed water. They were then heated to 550 °C with a heating rate of 15 °C/min under an air atmosphere. To determine the mass of adsorbed organic molecules, the weight loss was measured in the temperature range from 200 °C to 400 °C, using a tangential baseline correction.

*Adsorption of N-alkylammonium salts:*

To a sample of 50-70 mg of delaminated mica 3 ml of an ethanolic solution of ammonium salt (0.1 M) was added. After 24 h at 65 °C the samples were centrifuged and the supernatant solution decanted. This procedure was repeated (including treatment with ammonium salt). After filtration, a procedure of centrifugation, suspending and washing with 3 ml pure ethanol (puriss.) was repeated three times. The remaining ethanolic suspension of the mica was used to prepare a powder sample (as below) for X-ray diffraction analysis.

*Mixtures of ethanol and water*

The previously reported studies were carried out in aqueous solution by dissolving cation- terminated poly(ethylene glycol) in water. To determine the factors influencing the brush formation, we used high grade ethanol and glycol (puriss, Fluka, Buchs, Switzerland). In the case of ethanol, we prepared mixtures of ethanol/water with the following w/w ratios: 0/100, 85/15, 70/30, 50/50, 30/70, 15/85, 100/0. For each particular mixture of ethanol and water, the complete ion exchange isotherm was determined following the procedure described above.
Mixtures of glycol and water

In the case of glycol, only glycol/water w/w with ratios up to 50/50 have been investigated: 0/100, 30/70 and 50/50. All experiments were carried out with a solution concentration of cation-terminated poly(ethylene glycol) of about 0.5 mM for the poly(ethylene glycol) with a degree of polymerization of $\chi=47, 117, \text{and } 234$. In all cases, the preparation of the solutions was accomplished by using ultrasound. Generally, the experiments were performed at an ambient temperature of 34°C.

Temperature-dependence

In the case of temperature-dependent studies of the ion-exchange process, we investigated the polymer brush formation at 50 and 70°C.

Externally added lithium bromide

The influence on the ion-exchange behavior of cation-terminated poly(ethylene glycol) of various molecular weights on lithium bromide was determined. The molar ratios of lithium bromide to PEG was 2, 7 and 14, respectively. Therefore, the amount of lithium bromide per reference area in $\mu\text{mol/m}^2$ exceeds the amount of cation-terminated poly(ethylene glycol) by a large amount. The lithium bromide used was supplied by Fluka, Switzerland, and was dried under vacuum at 100°C prior to use. The amount of polymer adsorbed on the surface was determined by thermogravimetric analysis (TGA) as described above.

Reference

Curriculum Vitae

Name: Michael Olaf Geke
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EDUCATION

12/1995 - present  FEDERAL INSTITUTE OF TECHNOLOGY Zurich, CH
Ph.D. thesis at the Institute of Polymers supervised by Prof. U.W. Suter.

Diploma thesis supervised by Prof. R.R. Schmidt, Department of Organic Chemistry, Konstanz.

10/1990 - 05/1995 UNIVERSITY OF KONSTANZ Konstanz, FRG
Chemistry studies with specialisation in organic-, computational- and biochemistry.

Awards / Memberships / Scholarships

- Awarded the Diploma Prize of the University of Konstanz for the best levels of the year, Konstanz (1995)
- Awarded a grant of the Deutsche Sporthilfe e.V., Frankfurt a.M., for professionals in sports. (1985-1987)
- Member of the German Chemical Society (GDCh) E.V., Frankfurt a.M.(1992)
• Member of the American Chemical Society (ACS) (1997)
• Participant at the International Chemistry Olympiade (1990)

Professional and Teaching Experience

1991-1993 Teaching assistant for organic chemistry at the University of Konstanz
1995-1997 Assistant at the Department of Material Science, ETH

Sports

• Ranked at fifth position at the World Championships in Sailing (X99) in 1995.
• Member of the German Sailing Team (AEROSAIL).
• Member of the Youth National Team in Volleyball; participated at several international contests.
• Supervised and trained beginners as well as professionals in sailing and in volleyball.