Mechanically linked oligorotaxanes

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7 Interaction forces in dibenzyl-ammonium–crownether pseudorotaxanes

7.1 Introduction

Since the discovery of inclusion complexes, chemists have provided us with thousands of different structures,\(^1\) which might be employed in the design of supramolecular architectures. To use self-assembly for the organization of molecules into complex devices, a good understanding of the interactions, which play a role in these complexes, is necessary. The complexation of macrocycles with (inorganic) cations has been studied extensively in order to understand the effect of macrocycle and guest parameters on the stability of the resulting complexes.\(^2\) This understanding can lead to the intelligent design of new macrocycles and to the prediction of their effectiveness to form complexes with guest species. Here, we will study the complexation behavior of crownethers with dibenzylammonium (DBA) ions, which are known to form inclusion complexes.

These pseudorotaxanes have already been studied with \(^1\)H-NMR spectroscopy to determine the association constant and X-ray studies have been performed on single crystals to establish their 3D structure.\(^3\) From the interatomic distances found in those crystals, assumptions have been made concerning the type of interactions present between the crownether and the secondary ammonium ion.

To obtain more detailed information on the complex formation between crownethers and DBA ions, we have employed Scanning Force Microscopy (SFM). In the SFM, the tip, covered with a self-assembled monolayer (SAM) of DBA ions, is brought into contact with a substrate bearing a crownether SAM. Pseudorotaxanes are created in situ. In a single measurement, the force needed to separate the two moieties of the complex, which is related to the dissociation constant, can be determined and a direct measurement of the type of interactions in the complex can be made. Since these measurements are performed in solution, a more realistic result is obtained, in comparison to the indirect X-ray studies of single crystals. Additionally, the use of monolayers eliminates the problem of solubility for the separate species, thus the complexation in any solvent or solvent mixture can be studied in this way.
The interfacial free energy of a certain tip–substrate combination can be derived from SFM measurements and gives an indication for the existence of specific interactions between the molecules in the monolayers.

In this chapter, we compared the interfacial free energy between DBA ions and two different crownethers of which one is cyclic (coronand, ‘closed’) and one is linear (podand, ‘open’). In this way, a proof was given that a complex between DBA and the ‘closed’ crownether is indeed formed during the SFM measurement.

The effect of different solvents on the adhesion force was investigated to determine the relationship between the solvent properties and the adhesion force between a DBA and ‘closed’ crownether monolayer. A comparison was made with association constants found in literature. Analysis of the force against different solvent properties by linear regression shows that the best correlation was found between the adhesion force and the Gibbs transfer energy of the DBA ion from water to the given solvent, hence the solvability of the ion.

Finally, the nature of the interacting forces between the crownether and DBA ion was measured directly from the long-range interactions between the DBA ions and the ‘closed’ crownether.

This chapter describes the determination of the interacting forces, which play a role in the complexation of rotaxane molecules, based on the DBA ion and crownethers. In the first part, a brief summary on studies on crownether complexes and a description of the force measurements is given. The next part describes the analysis of structural effects and solvent effects and the determination of the type of interactions present in DBA–crownether complexes.

### 7.2 dibenzylammonium–crownether complexes

#### 7.2.1 Structure in solid state

The structure of dibenzylammonium–crownether complexes (figure 7.1) has already been mentioned briefly in chapter 1.3.3. The secondary ammonium ion is threaded through the cavity of the crownether. As it was concluded from X-ray studies, the major interactions present are hydrogen bonds between the protons of the ammonium center and the adjacent methylene groups, and the polyether oxygen atoms of the crownether. Furthermore, electrostatic pole–dipole interactions as well as dispersive interactions such as π–π and/or CH–π interactions play a role in the complex.³,⁵
7.2.2 Structure in solution state

In a detailed study, the solvent effects on 18-crown-6 crownether complexes with inorganic ions (Li⁺, Na⁺, K⁺) have been described. In previous publications, the association constants have been reported to show direct or inverse correlations with the Gutmann donor number of different solvents. The Gutmann donor number provides a semiquantitative measurement of the ability of the solvent to donate its electrons into non-covalent bonds. Correlations with other solvent properties were also described, such as polarity, permittivity, solvation ability, Kirkwood parameter and dielectric constant. The best correlation for the association constant of the K⁺/18-crown-6 system was found with the standard Gibbs transfer energy of the potassium cation from water to the given solvent. In other words, the strength of the complex is determined by the solubility of the cation in the solvent used. In polar solvents such as DMF or hexamethylphosphorotriamide (HMPT), the potassium ion can readily dissolve and thus a low association constant is observed. In less polar solvents such as acetone or MeCN, the cation is poorly soluble and its complexation in the cavity of the crownether is energetically more favorable. The cation is ‘solvated’ in the crownether. Despite extensive studies on the complexation of cations in crownethers, no overall theory exists, which correlates the association constants with solvent properties.

The effect of a solvent on the association constant of the pseudorotaxane 7.1 has been discussed by Ashton et al. in 1995. In the 1H-NMR spectra of the pseudorotaxane in different solvents, signals for the complexed and uncomplexed species are observed. From their relative abundances, the association constants (Kₐ) and free energies of complexation (ΔG°) have been determined. The energies were found to vary from −15 to −25 kJ.mol⁻¹ (Kₐ = 27000 − 360). It was found that the association constants are dependent on solvent properties. In particular, a good correlation between the association constant and the Gutmann donor number was observed. Unfortunately, the authors give no explanation for the observed relation.
7.3 Determination of adhesion forces by means of SFM

To obtain a better understanding on the complexation of secondary ammonium ions with crownethers, it is necessary to get a direct observation of the interactions that hold the pseudorotaxane together. A possible technique for these measurements is SFM. It enables us to manipulate single molecules to form and break a complex and to determine directly the forces needed to break the complex. This has already been proven successful for the studies of interactions between inorganic surfaces, alkane monolayers with different lengths or different chemical end groups such as neutral, acidic/basic or chiral groups and for the study of interactions between biological samples.

The tip of the SFM and a substrate are covered with a monolayer of the two parts of the pseudorotaxane, DBA ion and crownether, respectively. When the tip is brought into contact with the substrate, the two moieties will interact and form a pseudorotaxane monolayer. Retraction of the tip from the surface breaks the pseudorotaxane complex and the separate components are exposed to the surrounding solvent. This process can be considered as the controlled dissociation of the pseudorotaxane into two dissolved species. A quantitative description of the nature of the interactions (ionic, hydrogen bonding, van der Waals) and the force needed to break the complex can be determined from the SFM adhesion force measurements.

For the measurement of the adhesion forces present between tip and substrate, the tip is kept at one position \((x, y)\) over the sample and only moved in the \(z\)-direction, i.e. perpendicular to the sample surface. The deflection of the cantilever is monitored as a function of the \(z\)-displacement. Via the spring constant of the cantilever, the deflection can be converted to a force. A typical measurement consists of two parts, the approach and retraction of the tip (figure 7.2) and the recorded deflection of the cantilever as a function of the tip–sample distance is called force–distance curve.

At a distance far away from the sample, the cantilever has no interaction with the sample and the force acting on the tip is zero (a). When the tip is approached, it will, at a certain distance from the sample, experience a long-range attractive force (b). This part of the curve contains information about the type of long-range interactions, which are present between tip and sample and which depend on the chemical nature of the two surfaces. At the point where the force gradient \((\delta F/\delta z)\) exceeds the spring constant of the cantilever, the tip will jump into contact (c). In contact, the cantilever will start to bend upward due to the repulsive contact forces (d) and the recorded force is proportional to the displacement.

Then the tip is retracted from the surface. The force will again be proportional to the displacement and can still maintain at a negative load due to attractive forces between tip and sample (e) until the load exceeds the adhesion force and the tip jumps out of contact (f). The measured adhesion force \(F_{\text{adh}}\) between the tip and sample is the force needed to separate the
two surfaces. As will be discussed later, the force can be related to the surface and interfacial free energies.

![Schematic representation of a force–distance curve, measured with SFM.](image)

**Figure 7.2.** Schematic representation of a force–distance curve, measured with SFM.

### 7.4 Results and discussion

To study the interactions between dibenzo-24-crown-8 and the dibenzylammonium (DBA) ion, monolayers were prepared with the thioether-functionalized species 7.2, 7.3 and 7.4 (figure 7.3). Besides the thiols and disulfides, thioethers are another class of organic sulfur compounds, which are known to form reasonably stable monolayers on gold, be it in a relatively disordered structure.22 The SFM-tip was coated with a monolayer of the ammonium ion 7.2 and substrates with either the ‘closed’ or ‘open’ crownether (7.3 and 7.4, respectively) were prepared.

![Structure of the studied compounds. Dibenzylammonium ion 7.2, the ‘closed’ crownether 7.3 and the ‘open’ crownether 7.4.](image)

**Figure 7.3.** Structure of the studied compounds. Dibenzylammonium ion 7.2, the ‘closed’ crownether 7.3 and the ‘open’ crownether 7.4.
The complexation between the dibenzylammonium ion 7.2 and the ‘closed’ crownether 7.3 has already been studied by the determination of the association constants in solution.³ To verify whether the interactions measured in the SFM are solely due to the functional groups or also due to structural effects, the complexation between the dibenzylammonium ion 7.2 and the ‘open’ crownether 7.4 was compared with the complexation between 7.2 and the ‘closed’ crownether 7.3. In case a structural recognition is present, the complexation with the ‘closed’ crownether should be stronger than for the dibenzylammonium ion–‘open’ crownether complex, hence a higher adhesion force should be found.

7.4.1 Structural effects

To give a quantitative description of the interactions, which are present between the DBA-tip and the crownether-substrates, we have determined the surface and interfacial free energies for the different compounds in ethanol. The retraction part of a typical force–distance curve for the DBA–‘closed’ crownether system in ethanol is shown in figure 7.4. An average adhesion force was determined by taking the results of at least 30 measurements.

![Figure 7.4. Typical force–distance curve for a dibenzylammonium ion-tip and a ‘closed’ crownether-substrate in ethanol.](image)

As shown in previous studies,¹⁷ a good approximation for the work of adhesion determined by SFM can be calculated from the Johnson–Kendal–Roberts (JKR) theory, where two solids adhere via short-range adhesion forces, forming a connecting neck.²³ The adhesion force is given by the following relation:
\[ F_{ad} = -\frac{3}{2} \pi R W_{12} \]  

(1)

where \( R \) is the radius of curvature of the tip and \( W_{12} \) is the work of adhesion needed to pull the tip off the sample. \( W_{12} \) can be expressed in terms of surface free energies:

\[ W_{12} = \gamma_{13} + \gamma_{23} - \gamma_{12} \]  

(2)

where \( \gamma_{13} \) is the tip surface free energy in equilibrium with the medium, \( \gamma_{23} \) is the substrate surface free energy in equilibrium with the medium and \( \gamma_{12} \) is the interfacial free energy of the tip–substrate contact interface. For identical tip–substrate combinations, e.g. DBA–DBA, the work of cohesion is: \( W_{12} = 2\gamma \), where \( \gamma = \gamma_{13} = \gamma_{23} \), is the surface free energy of the particular surface against the medium. The interfacial free energy \( \gamma_{12} \) is zero. For each compound we have determined this surface free energy (table 7.1, rows 1–3).

Subsequently, the work of adhesion for the DBA–‘closed’ crownether and DBA–‘open’ crownether system has been determined. After substitution of the surface free energies in equation (2), the interfacial free energy can be calculated for both systems. Table 7.1 shows the free energies as determined in ethanol.

<table>
<thead>
<tr>
<th></th>
<th>Surface free energy</th>
<th>Interfacial free energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \gamma_{13} ) (mJ.m(^{-2}))</td>
<td>( \gamma_{12} ) (mJ.m(^{-2}))</td>
</tr>
<tr>
<td>DBA</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>‘closed’ crownether</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>‘open’ crownether</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>DBA–‘closed’ crownether</td>
<td></td>
<td>–1.6</td>
</tr>
<tr>
<td>DBA–‘open’ crownether</td>
<td></td>
<td>–0.3</td>
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</table>

For the DBA–‘closed’ crownether system an interfacial free energy of \(-1.6 \text{ mJ.m}^{-2}\) was obtained, for the DBA–‘open’ crownether it is only \(-0.3 \text{ mJ.m}^{-2}\). A more negative value indicates a stronger preference for the two compounds to mix.\(^\dagger\) We can conclude from the interfacial free energies that the dibenzylammonium ion forms a stronger complex with the ‘closed’ crownether than with the ‘open’ crownether, as a larger energy is required to separate

\(^\dagger\) The interfacial energy is defined for two coexisting phases at equilibrium. A value of the interfacial energy less than zero means that these phases would mix. Thus, in practice, \( \gamma \) values smaller than zero are not found. However, in our measurement the two molecular layers on the tip and substrate cannot mix due to the tethering of the molecules, which results in the measurement of negative \( \gamma \) values [S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces and Membranes*, Addison-Wesley Publishing Company, New York, 1994].
the two surfaces. This indicates that the molecular recognition of the DBA ion by the crownether is strongly influenced by the preorganized shape of the ‘closed’ crownether.

Similar results have also been found in studies of the complexation of 18-crown-6 and its acyclic analogue pentaethylene glycol dimethyl ether with Na\(^+\), K\(^+\) and BuNH\(_3\)+ ions.\(^{24}\) In all cases, an approximately 10\(^4\)-fold drop in complexation constant was observed on going from the cyclic to the acyclic compound. This discrepancy, which results form geometric constraints on ring closure, is denoted as the ‘macrocyclic effect’.\(^{25,26}\) Its origin lies in a combination of ligand solvation effects and thermodynamic parameters (enthalpy and entropy).\(^{27}\)

### 7.4.2 Solvent effects

By means of Scanning Force Microscopy, we have been able to create and break in situ complexes between the two species of a pseudorotaxane. Encouraged by these results, we have attempted to extend these measurements even further. As discussed in § 7.2.2, the solvent has a strong influence on the association constants of crownethers with cations. In general, a more polar solvent will lead to a lower \(K_a\) and a resulting lower Gibbs free energy. By the measurement of the adhesion forces between a dibenzylammonium ion-tip and a ‘closed’ crownether-substrate, we have first attempted to find the same effect of solvent on the adhesion force as on \(K_a\). Performing the SFM measurements in a less polar solvent, where the association constant is larger, should lead to a higher adhesion force because the complexed state will be preferred over the dissociated state.

Adhesion forces for the DBA–‘closed’ crownether complex were measured in different solvents. At least 30 force–distance curves were taken for each measurement. In figure 7.5, the forces are plotted against several solvent properties, Gutmann donor number (DN), dielectric constant, solvent polarity and a normalized Gibbs transfer energy of the dibenzylammonium cation from water to the given solvent, \(\Delta G^\circ\). The Gibbs transfer energy is directly related to the Gibbs free energy of solvation \(\Delta G^\circ_{\text{solv}},\) which can be estimated by the Born equation:

\[
\Delta G^\circ_{\text{solv}} = -\frac{z^2 e^2 N_a}{8\pi\varepsilon_0 r_i} \left(1 - \frac{1}{\varepsilon_r}\right)
\]

\(^{†}\) Combination of the equations for the Gibbs energy of solvation of the ion in water (\(\Delta G^\circ_{\text{water}} = \mu^\circ_{\text{water}} - \mu^\circ_{\text{gas}}\)) and the Gibbs energy of transfer of the ion from water to the solvent S (\(\Delta G^\circ_{\text{water},S_{\text{solv}}} = \mu^\circ_{\text{solv}} - \mu^\circ_{\text{water}}\)) shows that both energies are related as \(\Delta G^\circ_{\text{water},S_{\text{solv}}} = \Delta G^\circ_{\text{solv}} - \Delta G^\circ_{\text{water}},\) the latter is a constant for the solvation of the DBA ion in water [Y. Marcus, *Ion Solvation*, Wiley & Son, Chichester, New York, 1985, p. 150].
where \( z_i \) is the charge number, \( r_i \) is the radius of the ion and \( \varepsilon_r \) is the relative dielectric constant of the solvent. The radius \( r_i \) is unknown but constant in all measurements. In the plot, a normalized Gibbs transfer energy is used:

\[
\Delta G^* = \frac{\Delta G_{\text{solv}}}{A}
\]

where \( A \) is constant. The used solvents are cyclohexane, dioxane, ethylacetate, 2-butanol, 2-propanol, ethanol and methanol.

![Graphs](image)

**Figure 7.5.** Relation between the adhesion force for the DBA ion–‘closed’ crownether system and different solvent properties: a) Gutmann donor number, b) solvent polarity, c) dielectric constant, d) normalized Gibbs transfer energy of the DBA ion.

The decrease in adhesion force (association constant) with an increasing DN (figure 7.5a) has also been observed by NMR studies. A solvent with a larger DN shows a stronger ability to compete with the ligands for the DBA cation, hence the energy loss to break the DBA–crownether bonds and create the DBA–solvent interactions is smaller compared to a solvent with a low DN number. The solvent polarity and dielectric constant (figures 7.5b and c) are related to the dipole moment of the solvent molecules. Solvents with a larger dipole can stabilize a charge more easily by virtue of its dielectric effect. Thus, a more polar solvent results in a larger gain in the DBA–solvent interaction energy, so that separation of the DBA from the crownether surface is more favorable, hence a smaller adhesion force is measured.
The Gibbs transfer energy (figure 7.5d) is related to the dielectric constant of the solvent, as shown in equations 3 and 4 and corresponds to the energy required to solvate the DBA ion. At lower values of $\Delta G^*$ (solvents with higher polarity) the ions are solvated more easily. Therefore it is favorable to dissociate the DBA ions from the crownether surface and ‘solvate’ them, hence a smaller adhesion force is found.

Linear fitting of the data shows a reasonable correlation of the adhesion forces against the Gutmann donor number, dielectric constant and solvent polarity with correlation coefficients between 0.64 and 0.82. The best correlation with $R = 0.94$ is found with the Gibbs transfer energy $\Delta G^*$. These results are similar to earlier studies on the complexation of potassium ions with 18-crown-6.\(^6\) Thus, it can be concluded that the adhesion forces, measured by means of SFM give a good indication of the complexation behavior of the DBA–‘close’ crownether system in solution.

In all plots in figure 7.5, measurements done in ethylacetate and 2-butanol deviate significantly from the linear fit. Correlation coefficients calculated without these points range from 0.91 to 0.99 for all solvent properties. To give a qualitative explanation for these deviations, we have compared these results with the adhesion forces determined for the DBA–DBA and the crownether–crownether systems. The former (figure 7.6) shows a fairly good linear relation ($R = 0.91$), indicating that the adhesion force between a DBA-tip and a DBA-substrate is dependent on the Gibbs transfer energy. In low polarity solvents, the ion–solvent interaction (‘solvation’) is less favorable and the ions on the tip and substrate prefer to interact with each other. The force needed to retract the tip from the substrate is thus stronger and \textit{vice versa}.

\textbf{Figure 7.6.} Adhesion force between a DBA-tip and a DBA-substrate in different solvents, plotted as a function of the normalized Gibbs transfer energy.

Determination of the adhesion forces between a crownether-tip and a crownether-substrate shows a dependency with the dielectric constant, comparable to the DBA–
crownether system. Again, the same two solvents (ethylacetate and 2-butanol), as well as 2-propanol, show a significant lower adhesion force than the others, indicating that it is favorable to create crownether–solvent interactions, in these particular solvents, hence that the force needed to retract the tip from the substrate is low. This can also explain the lower adhesion forces in these three solvents for the DBA–crownether system.

Figure 7.7. Adhesion force between a ‘closed’ crownether-tip and a ‘closed’ crownether-substrate in different solvents, plotted as a function of the dielectric constant.

The adhesion forces for the DBA–crownether system are a combination of two effects. First, there is a strong interacting force between the dibenzylammonium ion and the crownether. This force is in principle independent of the solvent. The nature of this interaction will be discussed later. Second, the solvation of the DBA ion and of the crownether, when the tip is retracted, leads to the solvent dependency. For both moieties, the adhesion forces are smaller when more polar solvents are used due to stronger interactions with the solvent (solvation). In addition, a deviation is observed for ethylacetate and 2-butanol, apparently due to very strong interactions with the crownether. The nature of these interactions is not clear but might be related to the size of the solvent molecules compared to the cavity size of the crownether, such as the ‘lock and key’ principle, conformation changes in the crownether or specific interactions between the solvent and the crownether, such as hydrogen bonding.

We have seen that the SFM can be used to measure the rupture of DBA–crownether complexes and that the necessary force depends on solvent properties in a similar way as the association constant. The next step is to quantify these forces to determine the association constant $K_a$ and is an important issue in the characterization of complexes. According to the JKR theory, the adhesion force is related to the work of adhesion (equation 1), which can be described as the energy difference between the associated and dissociated state of the complex. The work of adhesion should therefore be equal to the energy barrier determined from $K_a$ from potentiometry or NMR measurements via the Arrhenius equation. Since the Gibbs free energy is a state function (the energy difference between two states is independent
of the followed pathway), it should be possible to determine $K_a$ quantitatively from the SFM measurements.

The work of adhesion for the DBA–‘closed’ crownether system was determined from the adhesion force and the tip radius by the JKR theory. A typical value of $-6.4 \text{ mJ.m}^{-2}$ was found in dioxane. From molecular modeling, a surface area of ca. $55 \text{ Å}^2$ was found for the crownether molecules in a SAM, yielding a free energy of complexation of $-2.1 \text{ kJ.mol}^{-1}$. This is one order of magnitude lower than the values found by $^1$H-NMR. The reason for this might be that not all molecules in the monolayers form a complex. The unequivalent surface area of the DBA ions and crownethers lead to a mismatch for the complex. Thus, only a part of the molecules is in the correct position to actually form intermolecular interactions. The close packing of the molecules at the surface can result in a decrease of their entropy, which results in a smaller energy gain on complexation compared to in solution, hence a smaller adhesion force is measured. Moreover, the molecules, which do not form a complex, will still contribute for a small part to the total adhesion force via Van der Waals interactions. This makes a detailed analysis of the results and the determination of the association constant very difficult.

### 7.4.3 Type of interactions

To get more insight into the interactions between the DBA ion and ‘closed’ crownether during a force–distance measurement we can, besides the strength of the force, also determine the nature of the force. It is possible to distinguish between e.g. Van der Waals forces, dipole–dipole interactions or hydrogen bonding. Figure 7.8 shows two force–distance profiles of the tip-approach for the DBA–‘closed’ crownether system in ethanol and dioxane. Just before the jump-to-contact, the tip experiences a long-range interaction. The inset shows the double-logarithmic plot of this part of the curve. In both cases, a linear relationship is obtained with a coefficient of $-4.3$ for ethanol and $-4.7$ for dioxane. A coefficient of $-5$ would be expected for a dipole–ion interaction between the dibenzylammonium ion and the crownether. At first sight this result might contradict X-ray studies, which show predominantly hydrogen bonding between the methylene protons in the DBA ion and the oxygen atoms in the crownether. However, the measured interaction can also be considered as a combination of hydrogen bonding (coeff. = $-3$) and Van der Waals forces (coeff. = $-7$).

† In order to increase the mobility of the DBA and crownether molecules in the SAMs, mixed monolayers with 5–20% of the complexing molecules in a matrix of didodecylsulfide were used. Unfortunately, these samples did not show an increased adhesion force. In addition, the forces in different solvents showed only the hydrophobic interactions of the dodecyl chains.
Figure 7.8. Representative force–distance curves (approach) for the DBA-tip and ‘closed’ crownether-substrate measured in a) ethanol and b) dioxane. The insets show the double logarithmic plots of the force versus distance relationship just before the jump-to-contact.

Indeed, a good correlation is also found when the curves in ethanol and dioxane are fitted with two exponential decays with coefficients of –3 and –7, hence a combination of hydrogen bonding and Van der Waals interactions, which correlates with the previous studies.† Unfortunately, a detailed analysis to determine the contribution of the separate forces was not possible due to the noise in the SFM.

For the adhesion forces between the DBA ion-tip and the ‘open’ crownether-substrate, the measured forces in the approach curve were too small to derive any information concerning the present interactions.

We can conclude that, in both ethanol and dioxane, a combination of Van der Waals forces and hydrogen bonding play a role in the complexation behavior of the dibenzylammonium ion with the ‘closed’ crownether. Although the solvent (polar or nonpolar) can change the magnitude of the adhesion force as shown in the previous paragraph, the nature of the interactions remain the same.

7.5 Conclusions

The interacting forces between a tip covered with dibenzylammonium ions and surfaces with monolayers of either ‘closed’ (cyclic) or ‘open’ (acyclic) crownethers have been

† Fits with a combination of the coefficients –3 and –5 or with –5 and –7 gave less good correlations. A best fit with all three types of interactions (coeff. –3, –5 and –7) gave a repulsive ion–dipole interaction and should therefor be ignored.
measured by means of Scanning Force Microscopy. The structural effects in the crownethers on the complexation behavior have been determined by comparison of the ‘closed’ and ‘open’ crownether. From the adhesion forces measured in ethanol and the calculated interfacial free energies, it can be concluded that dibenzylammonium ions form significantly stronger complexes with ‘closed’ crownethers than with ‘open’ crownethers. This observation can be ascribed to the structural differences, hence the preorganized cyclic shape of the ‘closed’ crownether, also known as the ‘macrocyclic effect’.

A detailed study of the DBA ion–‘closed’ crownether system in different solvents shows a linear behavior between the adhesion force, which is related to the complexation energy, and the Gibbs free energy of transfer for the DBA ion from water to the given solvent, hence the solubility of the cation. Some correlation was also found with other solvent properties such as the Gutmann donor number, solvent polarity and dielectric constant, albeit less pronounced. Deviations were observed for ethylacetate and 2-butanol; remarkably low adhesion forces between DBA and the ‘closed’ crownether were found for these two solvents. The same deviation was also found in the adhesion forces between a ‘closed’ crownether-tip and a ‘closed’ crownether-substrate. Therefore, specific interactions between these solvent molecules and the crownether must be present.

Analysis of the long-range interactions in the DBA–‘closed’ crownether system showed that the interacting forces are most probably a combination of hydrogen bonding and Van der Waals interactions and no ion–dipole interactions. Similar results have also been concluded from X-ray studies of single crystals of a DBA–crownether complex.

We have shown that Scanning Force Microscopy can be used to determine the interactions in and the effect of solvent on DBA–crownether complexes. Although the association constant $K_a$ cannot be determined from these measurements, trends in the adhesion force vs solvent properties have been found, which are comparable to trends in the association constants of crownether complexes.

### 7.6 Experimental

**Materials**

All solvents were dried on molecular sieves for at least 24 hours prior to use. Gold wire (Schöne Edelmetallen) was 99.99 % pure. The thioether-functionalized dibenzylammonium hexafluorophosphate 7.2, ‘closed’ crownether 7.3 and ‘open’ crownether 7.4 were synthesized in the group of dr. J. Preece at the University of Birmingham, UK.
Au-coating of cantilever and sample substrates

Commercial Si$_3$N$_4$ cantilevers with integrated Si$_3$N$_4$ tip (Topometrix GmbH) were coated with a 75 nm gold layer, using a diffusion-pumped thermal evaporator (Edwards Auto 306). A layer of 2 nm of chromium was used as an adhesion promoter for gold. To prevent bending of the cantilevers, the backside was covered with a gold layer of 40 nm. Sample substrates were made from 1 × 1 cm$^2$ cut glass-slides, coated with 2 nm chromium as an adhesion promoter and 75 nm gold by thermal evaporation.

Chemical modification of cantilever and sample substrates

After gold deposition, the cantilevers and substrates were immersed in a 1 mM solution of the desired thioether in dichloromethane for at least 12 hours. Prior to use, the samples were rinsed thoroughly with dichloromethane and ethanol and dried in a stream of prepurified nitrogen gas.

Scanning Force Microscopy

The adhesion forces were measured on a Topometrix Explorer (TMX1010) SFM with an open liquid cell design. The pull-off rate was 0.1 µm s$^{-1}$. The spring constant (∼ 0.06 N m$^{-1}$) of the cantilevers was individually determined, using a non-destructive method described by Hutter and Bechhoeffer, which is implemented in the data-acquisition software of Topometrix. The average of at least 30 force–distance curves was determined for every measurement.

7.7 References


32. J. L. Hutter and J. Bechhoeffer, *Rev. Sci. Instrum.* 1993, 64, 1868; J. L. Hutter and J. Bechhoeffer, *Rev. Sci. Instrum.* (Erratum) 1993, 64, 3342. We used the corrected method by Butt et al., which accounts for the spatial distribution of thermal energy along the entire length of the cantilever. Furthermore, a correction factor of $\sqrt{4/3}$ is required in the most common case of a rectangular beam cantilever [H.-J. Butt and M. Jaschke, *Nanotechnology* 1995, 6, 1].