Characterizing NF and RO membrane surface heterogeneity using chemical force microscopy

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Abstract

Chemical force microscopy (CFM) was used to characterize the chemical heterogeneity of two commercially available nanofiltration and reverse osmosis membranes. CFM probes were modified with three different terminal functionalities: methyl (CH$_3$), carboxyl (COOH), and hydroxyl (OH). Chemically distinct information about the membrane surfaces was deduced based on differences in adhesion between the CFM probes and the membrane surfaces using both traditional atomic force microscopy (AFM) force measurements and spatially resolved friction images. Contact angle titration and streaming potential measurements provided general information about surface chemistry and potential, which largely complemented the CFM analyses, but could not match the accuracy of CFM on the atomic level. Using CFM it was found that both membranes were characterized as chemically heterogeneous. Specifically, membrane chemical heterogeneity became more significant as the scan size approached colloidal or micron-sized dimensions. In many instances, the chemically unique regions, contributing to the overall chemical heterogeneity of the membrane surface, were substantially different in chemistry (e.g., hydrophobicity) from that determined for the surface at large from contact angle and streaming potential analyses. Topographical and corresponding CFM images supports previous adhesion studies finding a correlation between surface roughness and the magnitude of adhesion measured with AFM. However, chemical specificity was also significant and in turn measurable with CFM. The implication of these findings for future membrane development is discussed.

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Keywords: Chemical force microscopy; Membrane; Chemical heterogeneity; AFM

1. Introduction

Accounting for physical and chemical heterogeneities on membrane surfaces is a significant hurdle when attempting to use thermodynamic models for describing interfacial interactions in membrane processes. All surfaces are heterogeneous in physical structure, charge, and functional group structure and chemistry. Physical heterogeneity (i.e., surface roughness) of membranes has been extensively studied by investigators attempting to understand and model its influence on interfacial interaction energies [1–5]. Although considerable advances have been made in this area, full agreement between theoretical and experimental results is yet to be realized. Even when roughness effects are considered, model predictions are orders of magnitude less than experimentally measured deposition and attachment efficiencies [6]. Presumably, this underestimation could result from a number of factors; however, surface chemical heterogeneity is most likely [7,8]. To date, the role of membrane chemical heterogeneity in membrane–solute interactions has received little attention, principally due to limitations in techniques available to study surface chemical heterogeneity.

Previous studies examining the role played by thermodynamic interactions in particle transport and deposition processes have found that particles tend to preferentially deposit onto specific locations on collector surfaces [1,6,8–10]. Although the source of this phenomenon is still speculative the presence of chemical heterogeneities on the collector surfaces is a promising explanation [1,6,8,10]. In studies modeling colloid transport through filter media, experimentally measured attachment efficiencies differ dramatically from theoretical predictions that assume homogeneous surface chemistry [7,8,11–13]. Indeed, deposition rates were found to be directly proportional to the propensity of chemically distinct areas (quantified in terms of chemical heterogeneity) on the collector surface. To the authors'
knowledge, similar studies have not been performed for deposition onto membrane surfaces. The chemical heterogeneity of water treatment membrane surfaces may potentially play a significant role in determining membrane performance and fouling behavior. In the initial stages of membrane fouling, particles in the smaller (<1 μm) size range deposit first and are followed by larger (>1 μm) particles [14]. Particles with dimensions less than 1 μm (colloids) are more influenced by thermodynamic forces than hydrodynamic forces because of their large surface area to volume ratio. And as colloid size decreases, membrane chemical heterogeneity has a greater effect in determining the overall interfacial interaction between the two surfaces [13]. This has been described in terms of a ratio of patch to particle size ($R_{patch}/R_{particle}$) where the patch represents an area on the membrane surface having a different chemistry than the surface at large [6]. As $R_{patch}/R_{particle}$ increases, the effect of membrane chemical heterogeneity on the interfacial interaction increases.

Until recently, limitations of the spatial resolution of surface characterization techniques have prevented detailed characterization of surface chemical heterogeneities. For example, contact angle analysis is commonly used to characterize membrane surface energy properties such as the apolar (van der Waals) and polar (acid–base) components [15–17]. However, contact angle measurements use a millimeter-sized water droplet that interacts with multiple surface groups [18]. A membrane’s electrical potential is typically determined using streaming potential measurements, which are often used to calculate zeta potential [19]. Streaming potential is a measure of the electrical potential difference created by the movement of ions across the charged surface. Consequently, streaming potential measurements provide an averaged zeta potential for the surface based on the bulk surface characteristics. Both of these techniques provide average values of the surface properties; neither allows for the evaluation of the distribution of properties across a membrane surface.

Recent advances with scanning probe microscopes, particularly the atomic force microscope (AFM), have provided a means by which a surface may be characterized with atomic-level resolution [19–24]. AFM has largely been used to characterize surface topography, but it may also be used to provide chemical information about a surface using force measurements. For example, by modifying the chemistry of an AFM probe, the spatial distribution of surface energy properties may be assessed. This technique is referred to as chemical force microscopy (CFM) [18,25]. CFM is a relatively new characterization tool that is capable of providing chemically specific information about a surface with nanometer-scale resolution based on changes in friction or adhesion between the AFM probe and the sample surface [22,24–26]. For topographic measurements an AFM operating in contact mode measures the vertical deflection of a cantilever as it scans across the surface, which corresponds to changes in height. However, in CFM both the vertical and lateral cantilever deflections are measured. The lateral deflection is indicative of changes in the adhesion between the probe and surface. Because adhesion or friction is a function of chemical interactions occurring between the two surfaces, chemically specific information may be determined about the surface, if the probe surface chemistry is well defined [25]. This may be accomplished by giving the probe a specific functionality (e.g., CH$_3$, OH, CF$_3$, or COOH) using a number of available techniques [26]. Therefore, combined with the sensitivity and resolution of AFM, CFM provides an avenue by which the physical and chemical heterogeneity of a surface may be simultaneously assessed. This information would serve as a critical check for the ability of characterization techniques based on less spatially specific assessments of surface properties to describe membrane-solute interactions.

The objective of this investigation is to compare the surface properties of several water treatment membrane surfaces determined from conventional characterization techniques (e.g., streaming potential and contact angle) to those elucidated from spatially resolved CFM images. Through these comparisons, the significance of membrane surface heterogeneities, specifically those of a chemical origin, will be elucidated. Additionally, the potential implications of these results with respect to solute transport and deposition in membrane processes are considered.

2. Materials and methods

2.1. Membranes

This investigation studied two commercially available reverse osmosis (RO) and nanofiltration (NF) membranes. The RO membrane selected for this investigation is the Osmonics (Minnetonka, MN) SG membrane; the NF membrane selected is the Osmonics HL membrane. Membrane samples were supplied as dry sheets and stored in doubly deionized water (DDW) at 5 °C. The SG and HL membranes were chosen for study because one is hydrophobic (the SG membrane) and one is hydrophilic (the HL membrane) and they are both relatively smooth [16]. Smoother surfaces are desired in order to isolate chemical heterogeneities from physical heterogeneities.

2.2. Membrane surface energy characterization

The membrane surfaces were characterized in terms of three surface energy contributions: electrostatic (EL), Lifshitz van der Waals (LW), and acid–base (AB) interaction. According to the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) model, the sum of these components describes the total interfacial free energy between two surfaces immersed in a liquid medium [17]. EL forces arise from the interactions between the electrical double layers, which surround surfaces. The apolar LW component is primarily a function of dispersion forces and is attractive for most systems. The polar AB component may be either attractive (hydrophobic) or repulsive (hydrophilic) [17] and is comprised of two non-additive parameters. These parameters are complementary in nature and are defined as the electron-acceptor ($\gamma^+$) and electron-donor ($\gamma^-$) surface energy components.

The EL interaction energy was calculated according to Hogg et al. [27] using measured zeta potential and assuming constant surface potential. Membrane zeta potential was determined using a streaming potential analyzer (ZetaCAD, CAD Instrumentation, Les Essarts Le ROI, France). Streaming potential was measured with a background electrolyte of 10 mM NaCl.
over a pH range of 3–9 at 25 °C. Zeta potential was calculated from the measured streaming potential using the Helmholtz-Smoluchowski equation with the Fairbrother and Mastin substitution [28]. The LW and AB surface energy properties were determined using the method outlined by van Oss [17]. Briefly, the LW and AB properties of a surface may be determined from the contact angles of two polar liquids and one apolar liquid on a solid surface. Surface free energy components were calculated from the measured contact angles using the Young-Dupré equation [17]:

\[ \gamma(1 + \cos \theta) = 2 \sqrt{\gamma_l^2 + \gamma_s^2 + \gamma_C^2} \]  

where \( \theta \) is the measured contact angle; \( \gamma_l^LW \) is the van der Waals free energy component (mJ/m²); and subscripts \( l \) and \( s \) designate the liquid and solid phases, respectively.

Contact angles on each membrane surface were measured for three well-characterized probe liquids: doubly deionized water (DDW), formamide, and bromonaphthalene. Receding contact angles were measured using the captive bubble technique for three well-characterized probe liquids: doubly deionized water (DDW), formamide, and bromonaphthalene. Receding contact angles were measured on no less than five membrane coupons for each sample resulting in a minimum of fifteen contact angles per membrane.

2.3. Membrane roughness analysis

All AFM experiments were carried out using a Park Scientific Instruments (Sunnyvale, CA) atomic force microscope. The atomic force microscope was operated in the contact mode using a quartz liquid cell. Silicon nitride microscopes with integrated pyramidal tips (VEECO Instruments, Sunnyvale, CA) were used to image membrane surface topography. The membrane surfaces were measured in tapping mode. Five separate scans, each covering an area of 100 \( \mu \)m², were acquired on each membrane to determine the spatial variability of surface roughness features. Roughness is reported as average roughness \( R_a \), root mean square roughness \( R_s \), and surface area difference (SAD). Following each test, the liquid cell was rinsed with DDW and blown dry using purified nitrogen.

2.4. Surface chemical analysis

AFM images were generated by recording traces of cantilever lateral deflection while the membrane was raster-scanned back and forth. Surface topography was measured by recording the vertical or normal deflection of the cantilever. In this manner, both surface topography and differences in adhesion were simultaneously measured. Because the magnitude of the scanned adhesion is linearly dependent on the applied load [26,29], a constant applied load was used during all AFM imaging tests. AFM images were acquired using an atomic force microscope. AFM and CFM measurements were carried out using unmodified and chemically modified silicon nitride pyramidal tips attached to the end of a V-shaped cantilever. Modified tips were functionalized with a SAM terminating in methyl (CH₃), carboxyl (COOH), or hydroxyl (OH) end groups (NovaSCAN Technologies, Ames, IA). In CFM imaging, the resolution is determined by the actual tip-sample contact area, which is a direct function of the radius of curvature of the tip [26]. Using sharpened silicon nitride tips, CFM resolution may approach 10 nm. According to the manufacturer (VEECO Instruments, Inc.), the tips used in this study had a radius of curvature between 10 and 80 nm. Scanning electron microscopy images of the tips revealed an average value of approximately 40 nm (±10%). Cantilevers with different spring constants \( k \) were used in this study. The stiff cantilever had a \( k = 0.12 \) N/m, while the softer cantilever had a \( k = 0.06 \) N/m as reported by the manufacturer (VEECO Instruments, Inc.). The two spring constants made it possible to sample a range of interaction forces that may otherwise have been undetectable. A single tip of each type was used to image both membranes to ensure that the spring constant and tip radius were constant.

3. Results and discussion

The calculated surface energy properties, including the van der Waals (\( \gamma_l^LW \)), electron-acceptor (\( \gamma_C^+ \)), electron-donor (\( \gamma_C^- \)), and interfacial free energy of interaction with water (\( \Delta G_{121} \)) of the membrane surfaces and CFM probe functionalities at pH 6 with no background electrolyte are reported in Table 1. The sign and magnitude of \( \Delta G_{121} \) is a quantitative measure of surface wettability [17]. A positive value indicates a hydrophilic surface while a negative value indicates a hydrophobic surface. The HL membrane, unmodified silicon nitride, carboxylated, and hydroxylated surfaces are characterized as hydrophilic, while the SG and methylated surfaces are characterized as hydrophobic based on their respective \( \Delta G_{121} \) values.

Membrane zeta potential as a function of pH is reported in Fig. 1. The HL membrane is positively charged at low pH values and becomes increasingly negatively charged at higher pH values. The HL membrane has an isoelectric point (IEP) of approximately 3.9. The SG membrane is negatively charged over the entire pH test range with little change (approximately 3 mV) as pH increases from 3 to 9. The IEP of interest for

<table>
<thead>
<tr>
<th>Surface</th>
<th>( \gamma_l^LW ) (mJ/m²)</th>
<th>( \gamma_C^+ ) (mJ/m²)</th>
<th>( \gamma_C^- ) (mJ/m²)</th>
<th>( \Delta G_{121} ) (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>25.73</td>
<td>7.06</td>
<td>27.59</td>
<td>1.61</td>
</tr>
<tr>
<td>SG</td>
<td>42.21</td>
<td>1.69</td>
<td>11.31</td>
<td>–31.99</td>
</tr>
<tr>
<td>SN</td>
<td>26.10</td>
<td>0</td>
<td>31.10</td>
<td>10.26</td>
</tr>
<tr>
<td>–CH₃</td>
<td>20.01</td>
<td>0.13</td>
<td>0.03</td>
<td>–91.28</td>
</tr>
<tr>
<td>–COOH</td>
<td>27.37</td>
<td>0.45</td>
<td>25.32</td>
<td>25.32</td>
</tr>
<tr>
<td>–OH</td>
<td>39.00</td>
<td>0</td>
<td>74.01</td>
<td>66.80</td>
</tr>
</tbody>
</table>

* SN represents an unmodified silicon nitride tip.
the CFM analyses (pH 6), the HL and SG membranes have zeta potentials of approximately −5 and −7 mV, respectively (Fig. 1). The shape of the zeta potential curve for the HL membrane indicates the presence of both acidic and basic functional groups on its surface. For the HL membrane the positive charge below the isoelectric point is attributed to the protonation of amine functional groups (NH2 → NH3+). As pH increases, the HL membrane acquires a more negative charge from the deprotonation of carboxyl functional groups (COOH → COO−). For the SG membrane, the relative independence of zeta potential from pH indicates that ionogenic functional groups are present at low concentrations on the membrane surface (Fig. 1). Hydrophobic surfaces are characterized by a lack of substantial concentrations of Lewis acid-base groups, which influence both surface charge and wettability [17]. This observation is further supported by the calculated surface energy components for the SG membrane (Table 1), which was characterized by small γ+ and γ− values.

AFM-generated roughness statistics for the HL and SG membranes are reported in Table 2. Both membrane surfaces are relatively smooth with small (<12 nm) Rq and Rq roughness values. The surface area difference (SAD) was greater for the SG membrane compared to that calculated for the HL membrane. The higher SAD value is indicative of the higher density of peak features on the SG surface compared to the HL surface, which was characterized by few features. Thus, the HL surface is considered to be more smooth than the SG surface (Table 2).

### Table 2

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Rq (nm)</th>
<th>Rq (nm)</th>
<th>SAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>7.25</td>
<td>10.07</td>
<td>0.7</td>
</tr>
<tr>
<td>SG</td>
<td>8.72</td>
<td>11.19</td>
<td>3.2</td>
</tr>
</tbody>
</table>

**Table 3** Measured force and calculated work of adhesion values for the AFM tip-sample systems investigated (r = 40 nm, F = 0.01 M NaCl; pH 6; T = 20°C).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>SN</th>
<th>CH3</th>
<th>COOH</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average measured adhesion* (nN)</td>
<td>0.01 ± 0.02</td>
<td>0.26 ± 0.36</td>
<td>0.11 ± 0.15</td>
<td>0.27 ± 0.56</td>
</tr>
<tr>
<td>SG</td>
<td>0.02 ± 0.06</td>
<td>17.22 ± 17.20</td>
<td>1.10 ± 0.90</td>
<td>2.89 ± 2.35</td>
</tr>
<tr>
<td>Experimental work of adhesion (mJ/m²)</td>
<td>0.05 ± 0.11</td>
<td>1.38 ± 0.91</td>
<td>0.58 ± 0.80</td>
<td>1.43 ± 1.07</td>
</tr>
<tr>
<td>SG</td>
<td>0.11 ± 0.52</td>
<td>91.35 ± 91.25</td>
<td>5.84 ± 4.79</td>
<td>15.33 ± 15.53</td>
</tr>
</tbody>
</table>

* Probe.

### 3.1. Membrane-probe adhesion

#### 3.1.1. Measured adhesion values

The distributions of measured adhesion values for each of the AFM probes on the HL and SG membrane surfaces are reported in Figs. 2 and 3, respectively. Each measured distribution was fit with a Gaussian distribution. Additionally, the mean adhesion and calculated work of adhesion (Wk), for each data set are reported in Table 3. Wk was calculated from the mean adhesion reported in Table 3 for each data set using the Johnson-Kendall-Roberts (JKR) theory for contact mechanics (FAD = −3/2πγkWk) [31].

The measured adhesion values between the unmodified silicon nitride tip and both the HL and SG membrane surfaces were characteristic weak (Table 3) and did not vary substantially across the area sampled on each membrane (Figs. 2a and 3a). The weak interaction measured for the unmodified silicon nitride tip is due to the low density of functional silanol groups on the tip surface [22,32,33]. Substantially larger interactions occurred between the three functionalized tips and the membrane surfaces, demonstrating the influence and significance of chemical interactions, as opposed to a simple Hertzian relationship [34], on the tip-sample adhesion. Overall, the adhesion for each tip was substantially weaker on the hydrophobic HL membrane than on the hydrophobic SG membrane. The weakest adhesion measured on both membranes occurred with the COOH-functionalized tip; the strongest adhesion occurred with the CH3-functionalized tip and the hydrophobic SG membrane. These results demonstrate the significance of hydrophobic interactions in determining the magnitude of adhesive interactions [35].

#### 3.1.2. Adhesion values from the literature

Literature values for AFM-measured FAD, determined under similar pH and electrolyte conditions as used in this investigation, for a range of relevant surface functionalities are reported in Table 4. The adhesion for an NH2–NH2 interaction was included in Table 4 to demonstrate the propensity of such groups to form strong adhesive bonds.

#### 3.1.3. Evaluation of measured adhesion values based on values from the literature

The reported adhesion is weakest between two ionized carboxylated surfaces, where electrostatic repulsion is signifi-
cant, and greatest between two methylated surfaces, which are uncharged and hydrophobic. The strength of adhesion measured between a surface and functionalized AFM tip can be directly correlated to the ionization state and hydrogen bonding capacity of the interacting groups \([22,26]\). Adhesion increases with increasing hydrogen bonding capability and decreasing electrostatic repulsion. For example, when carboxyl groups are protonated they have a stronger adhesion with other carboxyl groups in the same ionization state (i.e., COOH and COOH) as a result of hydrogen bonding interactions between the two groups. At pH less than 4, COOH groups are fully protonated; as pH increases, the carboxyl groups begin to dissociate, becoming fully ionized (COO\(^-\)) at pH greater than 7 \([26]\). Based on the contact angle titration analysis (Fig. 4) it was determined that at the pH used in this investigation (pH 6) approximately 80% of the terminal carboxyl groups were ionized (Fig. 5). For pH greater than 4, the strength of adhesion between protonated carboxyl groups decreases rapidly as they become ionized, through an increase in EL repulsion. In a pH range of 5–6 the strength of adhesion sharply increases between COO\(^-\) and OH groups, as a result of hydrogen bonds being formed between the oxygen and hydrogen atoms in the respective functional groups. Hydrophobic effects dominate the interaction between the CH\(_3\) and NH\(_2\) groups producing the substantially larger adhesion reported for

Table 4

<table>
<thead>
<tr>
<th>Interacting chemistry</th>
<th>(F_{\text{AD}}) (nN)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>COO(^-) (\rightarrow) COO(^-)</td>
<td>0.5–0.5</td>
<td>([18,25,26])</td>
</tr>
<tr>
<td>OH(^-) (\rightarrow) OH</td>
<td>1–5.5</td>
<td>([25,26,47])</td>
</tr>
<tr>
<td>CH(_3) (\rightarrow) CH(_3)</td>
<td>12.5–55</td>
<td>([25,47])</td>
</tr>
<tr>
<td>NH(_2) (\rightarrow) NH(_2)</td>
<td>3–28</td>
<td>([25,26,47])</td>
</tr>
<tr>
<td>COO(^-) (\rightarrow) OH</td>
<td>0.5</td>
<td>([25,26])</td>
</tr>
</tbody>
</table>

Fig. 2. Distribution of adhesion values measured on the HL membrane surface using (a) an unmodified silicon nitride tip, (b) a CH\(_3\)-functionalized tip, (c) a COOH-functionalized tip, and (d) an OH-functionalized tip \((I=0.01\text{ M NaCl}, \text{pH} 6.1, \text{and } T=20^\circ\text{C})\).
the interaction between these groups (Table 4). In this manner, carboxyl functionalized tips provide information regarding the presence of ionogenic groups while hydroxyl and methyl functionalized tips may be used to construct hydrophobicity and hydrophilicity maps of the sample surface [26]. Carboxyl groups become ionized (COOH → COO\(^-\)) under alkaline conditions (Fig. 6).

Comparing the literature values to the values measured in this investigation, several trends are evident. The relatively weak adhesion measured for the HL membrane indicates that few hydrophobic (e.g., NH\(_2\)) groups are present on the membrane surface. Instead, it is likely that ionized carboxyl groups (i.e., COO\(^-\)) are more abundant. For the SG membrane, however, the magnitude of the adhesion for the CH\(_3\)-functionalized tip indicates a stronger presence of hydrophobic (i.e., NH\(_2\)) groups on the surface. The relatively weak adhesion of the COOH-functionalized tip indicates a lack of ionized surface groups and the existence of groups capable of forming hydrogen bonds (e.g., OH, NH\(_2\), and CH\(_3\)) on the SG membrane surface. Although surface roughness certainly impacts the range of adhesion values measured in each case, a clear distinction between membranes and functionalized tips exists and falls within the ranges established by previous investigators.

3.1.4. Distribution of adhesion values

A greater distribution of adhesion values, for both the polar and apolar probes, was measured on the hydrophobic SG membrane compared to that measured on the hydrophilic HL membrane. The distribution of values in each data set (Figs. 2 and 3) is attributed to changes in the magnitude of \(W_A\) between the tip and membrane surface [25,26] and to roughness effects [18,19,36]. For surfaces characterized by a random distribution of functional groups, the contact area should contain a mixture of terminal functionalities yielding a statistical mixture of contributions to the pull-off force [22]. Thus, the distribution of adhesion values should be described by a Gaussian (i.e., normal) distribution.

Adhesion results were analyzed using the Shapiro-Wilk normality test to determine whether they could be described by a normal
distribution [37]. None of the results for either membrane could be described by a normal distribution at a significance level of 0.05. This indicates that the functionalities of the membrane surfaces are clustered and highly variable.

3.1.5. Effect of surface roughness on distribution of adhesion values

Surface roughness also contributes to the variation in adhesion values measured across the membrane surfaces [38–40]. Roughness effects become especially pronounced as the size of the topographic feature approaches that of the tip radius. The pyramidal tips (r = 40 nm) used in this study would therefore be sensitive to roughness on the membrane surfaces. As the AFM tip encounters roughness features on the surface, the magnitude of the resulting adhesion becomes a function of the contact area between the tip and sample surface [1,36]. In other words, as contact area increases, as in a surface depression, adhesion increases. Thus, changes in surface energy are not solely responsible for the distribution of adhesion values presented in Figs. 2 and 3 necessitating a more detailed analysis to better characterize the chemical heterogeneity of the membrane surfaces. Spatially resolved CFM images of the membrane surfaces provide a means by which the distribution of adhesion values can be analyzed with respect to surface morphology.

3.2. CFM imaging

An increase in friction as an AFM probe is scanned across a membrane surface corresponds to an increase in adhesion between the probe and the membrane surface [25]. Because the magnitude of the measured adhesion is a function of probe and membrane surface energetics it is possible to map the spatial distribution of membrane surface chemistry using CFM, where both normal and lateral deflection of the AFM cantilever are measured [25]. The normal deflection is used to measure changes in surface topography while the lateral deflection provides simultaneous information regarding changes in friction or surface energy (i.e., adhesion).

Topographical and corresponding adhesion images acquired using the methyl, carboxyl, and hydroxyl functionalized tips, are shown in Figs. 7 and 8 for the HL and SG membranes, respectively, and summarized in Table 5. For each probe, both surface topography and corresponding adhesion images are reported so that the relationship between topography and adhesion may be determined. Changes in image contrast represent differences in surface height and adhesion as the tip is scanned across the membrane surface. In the topographical images, darker colors indicate depressions while lighter shades indicate increasing surface elevation. For the adhesion images, darker colors indicate
areas of low adhesion while lighter shades indicate stronger adhesion. Three 100 $\mu$m$^2$ scans were conducted for each tip functionality to ensure that the results presented here are representative of the sample surface at large. Because the AFM tip had to be removed in order to insert a new tip with a different functionality it was not practical to analyze the exact same location on the membrane surface each time.

From Fig. 7, it can be seen that the topography of the HL membrane surface is characterized by sparsely dispersed asperity (i.e., peak-like) features. From Fig. 8, the SG membrane was

Fig. 7. Representative topographical and corresponding CFM images for the HL membrane acquired with a CH$_3$-, COOH-, and OH-functionalized tip ($d=0.01$ M NaCl, pH=6.1, and $T=20^\circ$C).
characterized by a much higher density of asperity features. This difference between the HL and SG membranes is confirmed by the larger SAD value for the SG membrane than the HL membrane (Table 4). In the topographical image shown for the SG membrane measured with the methyl-functionalized tip (Fig. 8a) a large oval shaped depression was measured. This appears to be a random defect in the membrane surface as similar features were not detected in any of the other scans collected with the methyl-
as was concluded by Eaton et al. [36], the increased adhesion in the available interaction area [46] and to DLVO forces acting area. This increased adhesion has been attributed to an increase of the polymer mixture. The measured adhesion in the dimples is a region composed of more or less a single constituent polymer the degree of chemical heterogeneity at smaller scales. The inter-
port and attachment to these surfaces, it is necessary to examine membrane surfaces in terms of its potential impact on colloid trans-
action between the tip and membrane surface. This may be manifested as either an increase or decrease in

Table 5

<table>
<thead>
<tr>
<th>Probe</th>
<th>High adhesion</th>
<th>Moderate adhesion</th>
<th>Low adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL membrane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl</td>
<td>5.2</td>
<td>88.0</td>
<td>6.8</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>93.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>7.8</td>
<td>88.9</td>
<td>3.3</td>
</tr>
<tr>
<td>SG membrane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl</td>
<td>5.1</td>
<td>22.2</td>
<td>72.7</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>93.0</td>
<td>6.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>0.3</td>
<td>21.7</td>
<td>78.0</td>
</tr>
</tbody>
</table>

Comparing the topographical and adhesion images reveals a clear relationship between surface topography and adhesion, as has been found in other similar investigations [38,40–44]. A larger adhesion was measured in surface depressions than on peak features. This point is most clearly illustrated for the interaction between the methylated probe and the SG mem-
brane (Fig. 8). Here, a much higher adhesion, indicated by the lighter color shade, was measured within the oval-shaped sur-
face depression than anywhere else in the sample area. Because the depression feature is several microns in length and width, and thus substantially larger than the AFM tip (r = 40 nm), the increased adhesion in this case cannot solely be attributed to an increase in contact area between the two surfaces. In turn, this indicates a chemically unique area on the membrane sur-
face that may be indicative of a polymer aggregate. Polymer aggregates that form during the casting process can contribute to both the physical and chemical heterogeneity of membrane surfaces. A previous investigation on chemical heterogeneity in thin-film polymer blends found that dimple features were formed by polymer aggregates [4,36,45]. A polymer aggregate is a region composed of more or less a single constituent polymer of the polymer mixture. The measured adhesion in the dimples may be calculated as a function of separation distance using the Langbein approximation [34]:

$$A_i = 2\pi a_i h$$  

where $A_i$ is the interaction area; $a_i$ is the particle radius; and $h$ is the surface to surface separation distance. In Fig. 9, $A_i$ as a func-
tion of $h$ is shown for three different particle radii (0.25, 0.5, and 1 µm) representing typical colloid sizes. The x- and y-axes are plotted on log scales to more clearly show the magnitude of the interaction area at short separation distances (<10 nm) where thermodynamic interactions are most prevalent. $A_i$ decreases in a linear fashion as the separation distance between the two surfaces decreases. Taking the 1 µm particle for example: at $h = 50$ nm, $A_i = 0.32$ µm$^2$, which decreases to $0.99 \times 10^{-3}$ µm$^2$ once contact occurs. Here, contact is said to occur when $h = 0.157$ nm [17,34]. Thus, as the colloid approaches the membrane surface it interacts with an increasingly smaller area on the surface. Disregarding the influence of surface roughness effects, as the colloidal particle approaches the chemically heterogeneous surface the type of interaction it encounters will change due to the reduced surface area that it is interacting with. This may be manifested as either an increase or decrease in
Fig. 10. (a) Topographical rendering of the HL membrane surface, where the particular area of interest is bound by the white box. (b) CFM images of the bound area on the HL membrane surface corresponding to an interaction area and separation distance of 0.824 \( \mu \text{m}^2 \) and 60 nm, (c) 0.238 \( \mu \text{m}^2 \) and 30 nm, and (d) 0.044 \( \mu \text{m}^2 \) and 1 nm, respectively.
reductive or attractive forces or a reversal in the interaction completely. Therefore, the interaction on approach for a colloid to a membrane surface may not simply be described by a single force curve calculated based on the average properties of the membrane surface. In order to further explore this hypothesis it is useful to examine how surface hydrophobicity, and in turn hydrophobic attraction and hydrophilic repulsion, change as a function of h and A.

Fig. 10 shows several CFM images for an area on the HL membrane surface measured using the CH3 functionalized tip at increasingly smaller interaction areas. As previously mentioned, the adhesion image generated with the CH3 tip may be used to discern between hydrophobic and hydrophilic areas on the membrane surface. The top image (Fig. 10a) is a topographical rendering of the HL surface with the area of interest highlighted by the white box. Fig. 10b, c and d represent CFM images of the area of interest at increasingly higher magnifications (i.e., smaller interaction areas). Here, changes in adhesion are represented using a color scale where blue colors indicate areas of low adhesion for by contact angle analysis.

For A = 0.824 μm² the interaction is primarily characterized by moderate adhesion strength with some degree of high and low adhesion (Fig. 10b). Therefore, most of the region is characterized as weakly hydrophobic. For A = 0.238 μm² (Fig. 10c), the interaction is generally characterized by high to moderate adhesion, indicating hydrophobic attraction in the reduced sample area. Finally, for an A = 0.044 μm² (Fig. 10d) the interaction is characterized by low to moderate adhesion. Taking the adhesion strength as a measure of surface hydrophobicity, an approaching colloid would experience a range of interactions as it approached the membrane surface. Although this is a general observation, it provides preliminary evidence towards the potential impact on transport interactions. Therefore, surface chemical heterogeneities are significant and must be considered in solute both transport and deposition phenomena.

4. Conclusions

In order to realistically apply thermodynamic models to describe interactions at water treatment membrane interfaces, the distribution of both physical and chemical properties must be taken into account. AFM is now widely used and accepted as a viable method to characterize membrane surface roughness. In this investigation the AFM, operating as a CFM, may also be used to characterize the spatial distribution of membrane surface energetics. Based on the CFM analysis of the commercially available membranes studied here, several conclusions may be drawn. CFM may be used to identify and map the functionality of water treatment membrane surfaces and may thus be used to provide a more complete understanding of a membrane’s fouling propensity and to more precisely configure (e.g., polymer selection) future membrane development. Membrane surfaces are chemically heterogeneous on such a scale as to impact colloid transport and attachment processes, and membrane surface character is a function of both surface morphology and surface chemistry. On the colloidal scale (d ≤ 1 μm) membrane surface chemical heterogeneities are significant and in many cases, are dramatically different, chemically, from the surface chemistry determined using other characterization techniques (e.g., contact angle and streaming potential). Contact angle analysis accurately characterized the general hydrophobicity/hydrophilicity of the membrane surfaces, although the relative magnitude of surface hydrophobicity is highly variable based on AFM and CFM measurements, which is not accounted for by contact angle analysis.

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