Chapter 2

Hydrophobic Forces between Mica Surfaces in Aqueous Solutions of a Secondary Amine

2.1 Introduction

The DLVO theory states that the interaction force \( F \) between lyophobic particles in aqueous media can be expressed as a sum of the electrical double layer force \( F_e \) and the van der Waals force \( F_d \) (1, 2):

\[
F = F_e + F_d
\]  

(1)

However, Israelachvili and Pashley (3) observed that in \( 10^{-5} \) M cetyltrimethylammonium bromide (CTAB) solutions, the DLVO theory fails to predict the interaction forces between two cylindrical mica sheets at separation distances less than 5 nm. It was observed that, at such separations, the experimentally measured forces are more attractive than those predicted by Eq. [1]. This extra attractive force, termed as hydrophobic force \( F_h \), could be represented by a single exponential function as follows:

\[
F_h / R = C_o \exp(-H/D_o) 
\]  

(2)

where \( R \) is the mean radius of curvature of the interacting bodies, \( H \) the closest separation between the two curved surfaces, \( C_o \) a pre-exponential factor, and \( D_o \) is known as the decay length. The hydrophobic force observed by Israelachivili and Pashley at \( 10^{-5} \) M CTAB could be fitted to Eq. [2] with \( C_o = -30 \) mN/m and \( D_o = 1.0 \) nm.

Later investigators used different functional forms to represent hydrophobic forces. Claesson et al. (4) and Rabinovich and Derjaguin (5) showed that they can be expressed in the
form of a power law, which is of the same form as the van der Waals force:

\[
F_{h}/R = -K_{131}/6H^2
\]  

(3)

where \( K_{131} \) represents the hydrophobic force constant between two surfaces 1 across a medium 3. On the other hand, Christenson and Claesson (6) observed from their experiments that the hydrophobic forces measured between Langmuir-Blodgett (L-B) deposited monolayers of long-chain hydrocarbon and fluorocarbon surfactants on mica clearly follows a double-exponential force law:

\[
F_{h}/R = C_1 \exp(-H/D_1) + C_2 \exp(-H/D_2),
\]  

(4)

where \( C_1 \) and \( D_1 \) represent the short-range part of the interaction and \( C_2 \) and \( D_2 \) the long-range part. In this case, the values of \( D_1 \) and \( D_2 \) were observed to be in the range 2-3 nm and 13-16 nm, respectively.

Generally, depending on the magnitude of the decay lengths, hydrophobic forces may be classified into short-, medium- or long-range forces. When a decay length lies in the range 1-2 nm, it is referred to as short-range hydrophobic force. When it is in the range 2-10 nm, it is referred to as medium-range, while those in excess of 10 nm are referred to as long-range forces. Yoon and Ravishankar (7) plotted \( D_0 \) and \( D_2 \) of the hydrophobic forces measured by various investigators as a function of the advancing contact angle (\( \theta_a \)) of water on the substrate. It was found that the plotted data points could be divided into three distinct groups. The first group consists of the short-range hydrophobic forces observed with mica or silica surfaces coated with self-assembled monolayers of dodecylammonium hydrochloride (DAHCl) (8), CTAB (3) and dihexadecyldimethyl ammonium acetate (DHDAAM) (9), whose \( \theta_a < 90^\circ \). The second group consists of the long-range hydrophobic forces obtained with L-B deposited monolayers of hydrocarbons (6,10,11) and fluorocarbons (6) or chemically modified mica (12) and silica (13) surfaces, whose \( \theta_a > 90^\circ \). The third group consists of the mid-range hydrophobic forces obtained by Yoon and Ravishankar (7,14,15), who conducted force measurements between curved mica
surfaces in DAHCl solutions containing a neutral surfactant such as dodecylamine, octanol and dodecanol. The \( \theta_a \) of such surfaces was in the neighborhood of 90\(^\circ\). Thus, the data obtained by Yoon and Ravishankar (7,14) lie in the transition regime at \( \theta_a \approx 90^\circ \), below which hydrophobic forces are short-ranged and above which they become long-ranged.

Yoon and Ravishankar (7) proposed that when \( \theta_a \) approaches 90\(^\circ\), the packing density of the hydrocarbon chains on the surface starts to increase. Flinn et al. (16) showed that the fractional surface coverages of octadecyltrichlorosilane (ODTCS) on silica as measured by Fourier Transform Infrared Spectroscopy (FTIR) increases sharply from 0.17 to 1.0 as the equilibrium contact angle (\( \theta \)) increases from 84\(^\circ\) to 100\(^\circ\). Also, using atomic force microscopy (AFM), Flinn et al. (16) observed that ODTCS adsorsbs in the form of ellipsoidal patches (domains) on the silica surface and that as the surface coverage of ODTCS increases, the domains do not grow in size. Rather, the packing density inside each domain increases. It is well known that surfactant molecules adsorb on a substrate in the form of patches or hemi-micelles in order to maximize the interaction between hydrocarbon chains (17). Increase in packing density within the domains may have two important consequences regarding the hydrophobicity of the surface. First, the water molecules will be squeezed out of the monolayer, breaking the H-bond linkages between the surface and bulk water. Laskowski and Kitchner (18) suggested that the water film on a hydrophobic surface is unstable because of the deficiency of hydrogen bonding in the film. Second, due to close packing, the hydrocarbon chains begin take-up vertical orientations on the surface at \( \theta_a \approx 90^\circ \). As the hydrocarbon chains stand up, they expose an array of well ordered CH\(_3\) groups rather than CH\(_2\) groups toward the solution. According to Zisman (19), the critical surface tensions (\( \gamma_c \)) of the surfaces consisting of CH\(_3\) and CH\(_2\) groups are 23 and 31 mN/m, respectively. Thus, formation of close-packed domains of hydrocarbon chains should contribute to enhanced hydrophobicity.

The above theory may be useful in explaining why the decay lengths of the hydrophobic forces measured in DAHCl solutions are short-ranged, but increase in solutions containing both neutral surfactants. Although DAH\(^+\) molecules may adsorb in patches, they are not likely to be closely packed because their adsorption on the surface is site-specific. The DAH\(^+\) ions adsorbing
on mica occupy the sites vacated by the K⁺ ions, which are the centers of the oxygen hexagons whose area is 0.48 nm². Note, however, that this area is almost twice as large as the cross-sectional area of a hydrocarbon chain (≈0.20 nm²). Thus, the distance between two centers of adjacent oxygen hexagons is too large to allow for close packing of hydrocarbon chains. Moreover, it may be energetically unfavorable to form a close-packed monolayer of DAH⁺ ions because of the electrostatic repulsion between the charged ammonium head groups. On the other hand, neutral surfactant molecules such as dodecylamine can adsorb in between two DAH⁺ ions sitting at the centers of adjacent oxygen hexagons. This orientation is energetically favored because, as suggested by Gaudin and Fuerstenau (17), it should reduce the electrostatic repulsion between adjacent polar heads of the DAH⁺ ions adsorbing on the surface. Thus, the presence of neutral molecules increases the adsorbability of an ionic surfactant, thereby promoting the formation of domains of close-packed monolayers of surfactants. This is one explanation for the observation that $D_2$ increases in the presence of neutral surfactants.

In the present communication, a Surface Forces Apparatus (SFA) was used to further test the hypothesis that an increase in packing density should lead to the creation of longer-range hydrophobic forces. The measurements were conducted between mica surfaces in solutions of a double-chain secondary amine, i.e., dioctadecylammonium hydrochloride (DOAHCl). It was thought that the two hydrocarbon chains in each of the surfactant molecule should help increase the packing density of the hydrocarbon chains on the mica surface and, hence, create a hydrophobic force.

2.2 Experimental

2.2a Materials

DOAHCl of 99% purity was obtained from Aldrich Chemical Company and recrystallized from ethanol before use. Reagent-grade octanol from Fisher Scientific was used as received. Conductivity water was obtained from a Nanopure II water treatment unit and deareated for 3
hours before each experiment. Epoxy R Resin 1004 was obtained from Shell Chemical Co. The mica specimens used for direct force measurements were obtained from Unimica Corp., NY.

2.2b Methods

Two molecularly smooth mica surfaces were prepared by peeling mica sheets into micron-thin layers. The mica surfaces were silvered on one side by deposition of a 50 nm thick silver layer under high vacuum (6 to 10 torr). These surfaces were then glued silver side down onto cylindrical silica disks using Epon 1004 glue. Force measurements were conducted using a Mark-IV Surface Forces Apparatus from Anutech, Pty., which is similar to those of Tabor and Winterton (20) and Israelachvili and Adams (21). The separation distances between the two mica surfaces were measured using the multiple beam interferometry technique based on the method of fringes of equal chromatic order (FECO). The distances could be monitored to an accuracy of 0.2 nm, while the surface forces could be measured with a sensitivity of $10^{-8}$ N. The SFA was controlled using the SF-Scribe CV-78 software on a Macintosh computer.

The surface force measurements were conducted in Nanopure water at the beginning of every experimental run, and the results were compared with the literature values to ensure no contamination. In each experiment, the zero-distances were first measured in air and then in solution. However, the two distances were practically the same. A stock solution of $5 \times 10^{-3}$ M DOAHCl was prepared in 100% ethanol to ensure solubility. A $10^{-3}$ M stock solution of octanol was also prepared in 100% ethanol. Aliquots of the amine and octanol stock solutions were injected into the chamber of the SFA after separating the surfaces by 3-4 mm from the contact position. It should be noted that the ethanol concentration in any of the experiments never exceeded 1.5 % by volume. In DOAHCl solutions, the force measurements were commenced after 4 hrs of equilibration. In each experiment, the separation at which two mica surfaces jump into contact (jump distance), the force measured when two mica surfaces are separated from each other after contact (adhesion force) and the zero separation distance were also recorded. The radius of curvature at the point of contact was measured for each experimental run. At closer separations, surface forces were measured using the jump method. In this method, two surfaces
jump into contact when the slope of the force curve exceeds the spring constant of the cantilever spring. Changing the stiffness of the cantilever enables one to plot $d(F/R)/dH$ vs. $H$.

Surface tensions of solutions were measured using a Fisher Surface Tensiomat, which employs the du Nuoy method. The platinum-iridium ring used for surface tension measurements was washed in distilled water and flamed after each measurement. The surface tensiomat was calibrated against the surface tension data for ethanol-water solutions. Contact angle measurements were made using a Rame-Hart goniometer. Freshly cleaved mica surfaces were immersed in solutions of DOAHCl for a period of 1-2 hr. The mica pieces were then taken out and dried in a stream of nitrogen. Advancing ($\theta_a$) and receding angles ($\theta_r$) were measured using the sessile drop method with the same solutions in which they had been immersed.

2.3 Results

Figure 2.1 shows the surface tension vs. concentration curve for DOAHCl at natural pH. The surface tension of DOAHCl solution decreases with increasing concentration as expected. The critical micelle concentration (CMC) of the solution, as indicated by the arrow, is about 2.5x10^{-3} M. Also indicated in the figure by arrows are the CMC values for two other common single chain surfactants-octylammonium hydrochloride (OAHCl) and DAHCl. It is interesting to note that the CMC of DOAHCl lies between those of DAHCl (1.4x10^{-3} M) and OAHCl (0.5 M).

Fig. 2.2 shows the values of $\theta_a$ and $\theta_r$ of the surfactant solutions measured on the mica surfaces equilibrated in DOAHCl solutions. Both $\theta_a$ and $\theta_r$ increase with surfactant concentration suggesting that DOAH$^+$ ions adsorb on the mica surface rendering it hydrophobic. They reach a maximum at approximately 7x10^{-6} M. As the concentration increases further, $\theta_a$ remains constant while $\theta_r$ decreases. At concentrations<7x10^{-6}M, DOAH$^+$ ions adsorb on mica with a normal mode of orientation, i.e., with hydrocarbon tails oriented towards the solution phase. It appears that hydrocarbon tails form a close-packed monolayer at this concentration. There are two evidence for this. First, $\theta_a$ reaches as high as 90°, which is higher than obtained with single-chain
Figure 2.1. Surface tension ($\gamma_{lv}$) vs. concentration curve of DOAHCl solutions. Shown by the arrows are the critical micelle concentrations (CMCs) of DOAHCl, DAHCl and OAHCl.
Figure 2.2. Advancing ($\theta_a$) and receding ($\theta_r$) contact angles of mica sheets equilibrated in aqueous solutions containing varying concentrations of DOA$\text{HCl}$.
cationic surfactants like DAHCl (7). Second, $\theta_i$ decreases above this concentration, although $\theta_a$ remains unchanged. The decrease indicates that, at higher concentrations, DOAH$^+$ ions adsorb on top of the close-packed monolayer with the polar heads exposed toward the aqueous phase. Initially, the surfactant molecules in the second layer may lie flat, but at a concentration closer to the CMC of the surfactant, a bilayer is probably formed. As shown, $\theta_i$ is more sensitive than $\theta_a$ to the adsorption of the DOAH$^+$ ions in the second layer.

Fig 2.3 shows the results of force measurements conducted with two curved mica sheets in Nanopure water and at $5\times10^{-6}$M and $7\times10^{-6}$M DOAHCl. The measured forces (F) normalized by the radius of the sphere (R) are plotted as a function of the separation distance (H). The dashed and dotted lines represent theoretical fits to the experimental data using the constant charge and the constant potential models of the DLVO theory respectively. Table 2.1 shows the fitting parameters obtained using the algorithm of Chan et al. (23). The data obtained in Nanopure water can be fitted with $\psi_o$ (surface potential)=-163 mV and $\kappa^{-1}$ (Debye length)=96 nm. The van der Waals force was calculated using $A_{131}$ (Hamaker constant)=2.2x$10^{-20}$ J. These values agree well with those reported in literature (3, 8, 14, 15). The two surfaces jump into contact due to the van der Waals force at 4 nm. The adhesion (or pull-off) force (F(0)/R) between the two mica surfaces was measured to be 110 mN/m, which is also in agreement with the observations of other investigators (8, 14).

At $5\times10^{-6}$ M DOAHCl, the measured forces are less repulsive than those in Nanopure water, indicating that the mica surfaces are partly neutralized by the surfactant adsorption. The two surfaces jump into contact at H=14.1 nm, which is much farther out than that predicted by the DLVO theory, probably due to the presence of a hydrophobic force. The experimental data has been fitted to the extended DLVO theory:

$$F_t = F_e + F_d + F_h$$

which includes contributions from the hydrophobic force ($F_h$) in addition to those from $F_e$ and $F_d$. The parameters used to fit the experimental data are given in Table 2.1. $F_h$ was represented by a
Figure 2.3. $F/R$ vs. $H$ curves for the interaction between mica surfaces in (i) Nanopure water (●) (ii) $5\times10^{-6}$M DOAHCl (□) and (iii) $7\times10^{-6}$M DOAHCl (○). The dashed and dotted lines represent the constant potential and constant charge models of the DLVO theory respectively fitted to the force data. The thin solid line represents the vdw force obtained using $A_{131}=2.2\times10^{-20}$J. The thick solid line represents the extended DLVO theory incorporating a hydrophobic force term (Eq.[5]). The arrows indicate the positions at which the surfaces jump into adhesive contact.


<table>
<thead>
<tr>
<th>Amine (M)</th>
<th>Octanol (M)</th>
<th>$\theta_a$ (°)</th>
<th>$\theta_r$ (°)</th>
<th>$\psi_o$ (mV)</th>
<th>$C_1$ (mN/m)</th>
<th>$C_2$ (mN/m)</th>
<th>$D_1$ (nm)</th>
<th>$D_2$ (nm)</th>
<th>$r^*$ (nm)</th>
<th>$F(0)/R$ (mN/m)</th>
<th>$H_j^*$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>-165</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>110</td>
<td>4</td>
</tr>
<tr>
<td>5x10^-6</td>
<td>-</td>
<td>79</td>
<td>54</td>
<td>-73</td>
<td>50</td>
<td>-</td>
<td>2.2</td>
<td>-</td>
<td>0.75</td>
<td>235</td>
<td>14.1</td>
</tr>
<tr>
<td>5x10^-6</td>
<td>10^-7</td>
<td>79</td>
<td>54</td>
<td>-73</td>
<td>50</td>
<td>-</td>
<td>2.2</td>
<td>-</td>
<td>0.75</td>
<td>250</td>
<td>14.5</td>
</tr>
<tr>
<td>5x10^-6</td>
<td>10^-6</td>
<td>91</td>
<td>84</td>
<td>0</td>
<td>50</td>
<td>0.65</td>
<td>1.3</td>
<td>6.2</td>
<td>1.0</td>
<td>345</td>
<td>14.6</td>
</tr>
<tr>
<td>7x10^-6</td>
<td>-</td>
<td>90</td>
<td>81</td>
<td>0</td>
<td>50</td>
<td>0.65</td>
<td>1.3</td>
<td>5.1</td>
<td>0.9</td>
<td>330</td>
<td>9.2</td>
</tr>
<tr>
<td>7x10^-6</td>
<td>10^-7</td>
<td>89</td>
<td>81</td>
<td>0</td>
<td>50</td>
<td>0.65</td>
<td>1.3</td>
<td>5.2</td>
<td>0.9</td>
<td>330</td>
<td>10.1</td>
</tr>
<tr>
<td>7x10^-6</td>
<td>10^-6</td>
<td>73</td>
<td>66</td>
<td>62</td>
<td>50</td>
<td>-</td>
<td>1.7</td>
<td>-</td>
<td>1.2</td>
<td>310</td>
<td>12.2</td>
</tr>
<tr>
<td>2x10^-5</td>
<td>-</td>
<td>90</td>
<td>78</td>
<td>28</td>
<td>47</td>
<td>0.6</td>
<td>1.2</td>
<td>4.5</td>
<td>1.0</td>
<td>320</td>
<td>12.6</td>
</tr>
<tr>
<td>10^-4</td>
<td>-</td>
<td>83</td>
<td>52</td>
<td>135</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.65</td>
<td>70</td>
<td>2.7</td>
</tr>
</tbody>
</table>

*Adsorbed layer Thickness; *Jump Distance
single-exponential force law (Eq. [1]) with $C_0=-0.50$ mN/m and $D_0=2.2$ nm. (In the table, the parameters are given as $C_1$ and $D_1$ of Eq. [4] in order to be consistent with rest of the data.) The zero separation distance between the two mica surfaces has moved to 1.5 nm, which gives a value of 0.75 nm as the thickness of the adsorbed layer of DOAH$^+$ ions on each surface. The zero separation distance between the two mica surfaces has moved to 1.5 nm, which gives a value of 0.75 nm as the thickness of the adsorbed layer of DOAH$^+$ ions on each surface. Note here that the fully extended length of a DOAHCl molecule is $\approx 1.16$ nm. This was calculated using the following formula suggested by Tanford (25) for the length of a fully extended hydrocarbon chain ($l_c$):

$$l_c=(0.15 + 0.1265 \, n)$$  \hspace{1cm} (3)

where $n$ represents the number of hydrocarbon groups in the chain. Also, the value of $F(0)/R$ obtained at these condition is 235mN/m, which is substantially larger than that measured in Nanopure water.

At $7 \times 10^{-6}$ M DOAHCl, there is no evidence of repulsive forces at any separation distance. At $H<20$ nm, the measured forces are net attractive and are much larger in magnitude than the van der Waals forces. The two surfaces jump into contact at $H=9.2$ nm. The measured hydrophobic force is better represented using the double-exponential force law (Eq. [4]) rather than the single-exponential force law (Eq. [1]). It should be noted here that the hydrophobic forces measured with self-assembled monolayers of single-chain surfactants are usually represented by the single-exponential force law. The fact that the forces measured with DOAHCl requires a double-exponential force law indicates that the measured hydrophobic forces are stronger than those measured with the single-chain surfactants. The parameters that were used to fit the experimental data are given in Table 2.1. As shown in this table, the data were fitted with $\psi_0=0$ mV, $A_{131}=2.2 \times 10^{-20}$ J, $D_1=1.3$ nm and $D_2=5.1$ nm. The value $D_2$ is close to those obtained with DAHCl in the presence of octanol and dodecanol (7,14). The appearance of this long-range hydrophobic force may, therefore, be attributed to the likelihood that DOAHCl forms a close-packed monolayer on the mica surface. Since the data can be fitted with $\psi_0=0$, the concentration
of DOAHCl at which the surface force measurements were conducted should be considered as the point of charge reversal (p.c.r.) for mica in this surfactant solution. It should be noted here that surface forces measurements were also conducted at the same surfactant concentration at shorter separation distances using the jump (or gradient) method; however, the data will be presented in a later section and discussed.

It has been suggested that \( F(0)/R \) can be related to the interfacial tension (\( \gamma_d \)) as follows (24):

\[
F(0)/R = \alpha \gamma_d
\]  

(6)

where \( \alpha \) varies in the range of 3 to 4\( \pi \). Using the value of 330 mN/m obtained for \( F(0)/R \) at 7x10^{-6}M DOAHCl, one can that \( \gamma_d \) should lie in the range of 26.3 to 35 mN/m, which is close to the critical surface tension (\( \gamma_c \)) of hydrocarbon-coated surfaces (19).

Note that the adsorbed layer thickness increases from 0.75 to 0.9 nm as the concentration is increased from 5x10^{-6} to 7x10^{-6} M DOAHCl. This finding suggests that the packing density of hydrocarbon chains increases with surfactant concentration, which in turn causes the surfactant molecules to take up orientations that are closer to the surface normal.

Figure 2.4 shows the forces measured at 2x10^{-5} M DOAHCl. Also shown for comparison are the force data obtained at 7x10^{-6}M DOAHCl. As shown, the forces measured at 2x10^{-5} M DOAHCl are more repulsive, which suggests that the charge on the mica surface is probably reversed due to the adsorption of more DOAH^+ ions. The \( \psi_0 \) value used for the fit is 28 mV. It is likely that the additional DAH^+ ions are adsorbing in a second layer as evidenced by the fact that \( \theta_r \) reduces by 3° when compared to that at 7x10^{-6}M DOAHCl. Also, the adsorbed layer thickness is the same (0.9 nm) as that obtained at 7x10^{-6} M DOAHCl, which indicates that the DOAH^+ ions in the second layer lie flat on the top of the first monolayer. As has already been noted a complete bilayer formation may not be observed until the concentration is raised close to the CMC. It is interesting to note that at 2x10^{-5} M one can still see the presence of hydrophobic force, despite the
Figure 2.4. $F/R$ vs. $H$ curves for the interaction between mica surfaces in (i) $7 \times 10^{-6}$M DOAHCl (O) and (ii) $2 \times 10^{-5}$M DOAHCl (Δ). The dotted line represents the constant charge model of the DLVO theory fitted to the force data obtained at $2 \times 10^{-5}$M DOAHCl. The thin solid line represents the vdW force obtained using $A_{131}=2.2 \times 10^{-20}$J. The thick solid line represents the extended DLVO theory fitted to the force data (Eq.[5]). The arrows indicate the positions at which the surfaces jump into adhesive contact. The inset shows, on a larger scale, force data obtained at $1 \times 10^{-4}$M DOAHCl (●) in addition to those at $7 \times 10^{-6}$M (O) and $2 \times 10^{-5}$M (Δ). The dashed and dotted lines in the inset represent the constant potential and constant charge models of the DLVO theory respectively fitted to the force data.
fact that the measured force has become net positive. In fact, the hydrophobic force parameters are very similar to those obtained at 7×10⁻⁶ M DOAHCl. Also, the adhesion force measured at 5×10⁻⁶ M is very close to that in 7×10⁻⁶ M DOAHCl solution. These findings suggest that the adsorption density of surfactant molecules in the second layer is not very high, which is another evidence that the surfactant molecules adsorbing in the second layer may lie flat.

The inset in Figure 2.4 shows the force data obtained at 10⁻⁴ M DOAHCl along with those obtained at 7×10⁻⁶ M and 2×10⁻⁵ M at a larger scale. It can be seen that at the higher concentration, the surface forces become an order of magnitude larger than those at the lower concentration. The ψ₀ value used for the fit is 135 mV. Note also that the force data can be perfectly fitted to the DLVO theory. The two surfaces jump into contact at 2.7 nm, as predicted by the theory, due to the van der Waals force. Also, the adhesion force is only 73 mN/m. Thus, there is no evidence for a hydrophobic force.

The zero-separation distance is increased to 3.3 nm, which gives an adsorbed layer thickness of 1.65 nm. This value is much larger than the length of a fully extended DOAHCl molecule but is smaller than the thickness of a bilayer. It is possible, nevertheless, that some of the DOAH⁺ species adsorbing in the second layer are inversely orientated. The molecules adsorbing with inverse orientation may do so in patches, which could provide an explanation for the observation that contact angles remain high at 10⁻⁴ M DOAHCl (see Figure 2.2). If the patch-wise adsorption takes place in the second layer, part of the surface may remain hydrophobic. During contact angle measurement, three-phase contact may be formed along these hydrophobic patches, giving rise to large contact angles. However, the presence of patches of inversely oriented layer of DOAH⁺ ions may not be conducive to creating a hydrophobic force. Note also in Figure 2.2 that the contact angles show increasing degree of hysteresis with increasing surfactant concentration, which may be attributed to the roughness created by the patch-wise adsorption of DAH⁺ ions in the second layer.

In order to study the effect of coadsorption of octanol on the hydrophobic forces, force measurements were conducted with varying amounts of octanol at 5×10⁻⁶ M and 7×10⁻⁶ M
DOAHCl. Figure 2.5 shows the results of force measurements in solutions of $10^{-7}$ and $10^{-6}$M octanol and $5 \times 10^{-6}$ M DOAHCl. The uppermost force curve in the figure contains two sets of force data: one obtained at $5 \times 10^{-6}$ M DOAHCl and another at $5 \times 10^{-6}$ M DAHCl and $10^{-7}$ M octanol. Addition of $10^{-7}$ M octanol does not seem to have any effect on the surface forces. When the octanol concentration is increased $10^{-6}$ M, the repulsive force disappears. The force data are observed to be net attractive at all separation distances. The absence of double-layer repulsion indicates that the surfaces have been completely neutralized (i.e., $\psi_o = 0$ mV). This may be because the presence of octanol induces more DOAH$^+$ ions to adsorb on the mica surfaces. A similar observation was made by Yoon and Ravishankar for mica surfaces in solutions containing DAHCl and octanol. The hydrophobic force at $5 \times 10^{-6}$ M DOAHCl and $10^{-6}$ M octanol can be represented by Eq. [4] using $C_1 = 50$ mN/m, $D_1 = 1.3$ nm, $C_2 = 0.65$ mN/m and $D_2 = 6.2$ nm. These values are similar to those obtained at $7 \times 10^{-6}$ M DOAHCl without octanol. However, the $D_2$ value obtained in the presence of octanol is 1.2 times larger. This observation is in sharp contrast to those of Yoon and Ravishankar (6), who noted that, the $D_2$ value obtained between the mica surfaces in solutions containing both octanol and DAHCl is much larger (~5 times) than those in a solution containing DAHCl alone.

Figure 2.6 shows the effect of octanol on the surface forces at $7 \times 10^{-6}$ M DOAHCl. Recall that at $7 \times 10^{-6}$ M DOAHCl in the absence of octanol, mica surfaces are completely neutralized and the measured forces become net attractive. The lower force curve in Figure 2.6 suggests that addition of $10^{-7}$ M octanol does not have any effect on the surface force. This observation suggests that $10^{-7}$ M octanol does not significantly enhance the surface activity of DOAHCl. Even if it increases the surface activity a little, the hydrophobic force would not increase as the surface is completely covered by the DOAH$^+$ ions. When octanol concentration is increased to $10^{-6}$ M, however, the surface activity increases considerably and causes increased adsorption of DOAH$^+$ ions. However, the adsorption can occur only in the second layer with flat or possibly with inverse orientation in patches. This gives rise to the appearance of a repulsive force, as shown in Figure 2.6. The repulsive layer force can be fitted with $\psi_o = 62$ mV. Note that the two mica surfaces jump into contact at 12 nm, indicating the presence of a short-range hydrophobic force. It can be fitted by the single-exponential force law (Eq. [2]) with $D_o = 1.7$ nm. The thickness of the
Figure 2.5. $F/R$ vs. $H$ curves for the interaction between mica surfaces in $5 \times 10^{-6}$ M DOAHCl (O) and varying concentrations of octanol. The dotted line represents the constant charge model of the DLVO theory whereas the thin solid line represents the vdW force. The thick solid lines represent the extended DLVO theory (Eq.[5]).
Figure 2.6. $F/R$ vs. $H$ curves for the interaction between mica surfaces in $7 \times 10^{-6}$M DOAHCl (O) and varying concentrations of octanol. The dotted line represents the constant charge model of the DLVO theory whereas the thin solid line represents the vdW force. The thick solid lines represent the extended DLVO theory (Eq.[5]).
adsorption layer increases from 0.9 nm in the absence of octanol to 1.2 nm at $10^{-6}$ M octanol. The disappearance in long-range hydrophobic force and the increase in the adsorption layer thickness can be attributed to the adsorption of the DAH$^+$ ions in the second layer with polar head groups exposed towards the aqueous phase. The fact that the thickness of the adsorption layer remains well below the value expected of a bilayer, suggests that the DOAH$^+$ molecules are adsorbing in a second layer with flat orientation.

### 2.4 Discussion

In the present work, medium-range hydrophobic forces have been observed between mica surfaces in DOAHCl solutions in the absence and presence of octanol. Figure 2.7 compares the results obtained in the present work with those in literature. The results are given in the form of $\log\left[\frac{d(F/R)}{dH}\right]$ vs. H. The filled symbols represent the results obtained using the jump (or gradient) method, squares and circles representing those obtained at $7 \times 10^{-6}$ M DOAHCl and at $5 \times 10^{-6}$ M DOAHCl in the presence of $10^{-6}$ M octanol, respectively. The open symbols represent the data obtained at the same two concentrations using the equilibrium method. The equilibrium force data have been converted to $d(F/R)/dH$ data as follows. For every $F/R$ value at a given H, a set of constants $C_1$ and $C_2$ that can satisfy the equation are found:

\[
\frac{F}{R} = \frac{A_{131}}{6H^2} - \frac{C_1}{D_1} \exp\left(-\frac{H}{D_1}\right) - \frac{C_2}{D_2} \exp\left(-\frac{H}{D_2}\right)
\]

assuming that $D_1$ and $D_2$ values are the same as those shown in Table 2.1. These four parameters are, then, used to calculate the force gradient, $\log[d(F/R)/dH]$, using the following equation:

\[
\frac{d(F/R)}{dH} = \frac{A_{131}}{3H^3} + \frac{C_1}{D_1} \exp\left(-\frac{H}{D_1}\right) + \frac{C_2}{D_2} \exp\left(-\frac{H}{D_2}\right)
\]

It can be seen from Figure 2.7 that the data obtained using both the jump and equilibrium methods fall on the same curve. Also shown in Figure 2.7 for comparison are the Van der Waals force between bare mica surfaces in water; the hydrophobic forces measured between mica surfaces
Figure 2.7. Normalized force gradient data for the interaction between mica surfaces in 7x10^{-6} M DOAHCl (■, ) and 5x10^{-6} M DOAHCl + 10^{-6} M octanol (●, O). The solid and open symbols represent data obtained using the jump and equilibrium methods respectively. Also shown in the figures are the force gradients for the nonretarded van der Waals force (upper dotted line), force measurements between self-assembled monolayers of DAHCl and CTAB (thin straight line), DAHCl and octanol (dashed line) and L-B deposited monolayers of DDOAB (lower dotted line).
coated with self-assembled monolayers of CTAB (2), DAHCl (8), DAHCl and octanol (14); and that measured with mica surfaces coated with L-B monolayers of DDOAA (10). Three interesting observations can be made from the data shown in the figure. One, the hydrophobic force between DOAH⁺ monolayers is much stronger than those between DAH⁺ monolayers. Two, the strength of the hydrophobic attraction between DOAH⁺ monolayers is similar to that between mixed monolayers of DAH⁺ and octanol. Three, addition of octanol increases the hydrophobic force dramatically for the case of DAHCl whereas the increase is very small in the case of DOAHCl.

All of the above observations may be explained in terms of the changes in packing density of hydrocarbon chains on the surface as proposed by Yoon and Ravishankar (7). Here, packing density refers to the area occupied by each terminal methyl group. It was suggested that the sharp increase in hydrophobic force between DAH⁺ monolayers in the presence of octanol is due to the increased packing density of hydrocarbon chains, which in turn is a result of co-adsorption of octanol in the monolayer. Further, it was proposed that higher packing density may have two important consequences: i) water molecules are squeezed out from the monolayer, causing a breakage of the H-bond linkages between the surface and bulk water; and ii) exposure of an ordered array of CH₃ groups to the aqueous phase, which are known to be more hydrophobic than the CH₂ groups. Both of these factors should contribute to higher hydrophobicity of the mixed DAHCl-octanol monolayer, resulting in longer-range hydrophobic forces.

The surfactant used in the present work, i.e., DOAHCl, has two hydrocarbon chains attached to the amine group. Since each hydrocarbon chain occupies a minimum cross-sectional area of 0.2 nm², the area per DOAH⁺ molecule can be expected to be at least 0.4 nm². Note that this value is very close to the area occupied for each K⁺ ions on the mica surface, which is 0.48 nm². Therefore, it very likely that a close-packed monolayer can result if each DOAH⁺ molecule occupies the site vacated by the K⁺ ion on the mica surface. This can be seen from Figure 2.8a, which shows schematically how DOAH⁺ ions adsorb on mica. Compare this to Figure 2.8b, which shows the adsorption of DAH⁺ ions in mica. The cross-sectional area of a DAH⁺ molecule is ~0.2 nm², which is only one half of the area occupied by each K⁺ ion. This may be the reason...
Figure 2.8. Schematic representation of (a) $\text{DOAH}^+$ adsorbed on mica (b) $\text{DAH}^+$ on mica (c) $\text{DAH}^+$ and octanol on mica and (d) charge reversal in the presence of $\text{DOAH}^+$ and octanol.
why DAH$^+$ ions cannot adsorb to form a densely packed monolayer. Another consequence of this geometric misfit is that the surfactant molecules may be oriented at an inclination from the vertical position, producing a highly disordered monolayer of hydrocarbon chains. These may be part of the reason why hydrophobic forces between DAH$^+$ monolayers are much smaller than the case with the adsorption of DOAH$^+$ ions.

Neutral surfactants such octanol can co-adsorb in between the DAH$^+$ ions sitting at the centers of adjacent oxygen hexagons, which should in turn increase the packing density of hydrocarbon chains and, hence, cause the hydrocarbon tails to take up a more vertical orientation as shown in Figure 2.8c. This would expose an ordered array of CH$_3$ groups to the aqueous phase, which should help create longer-range hydrophobic forces.

When octanol is present in a DOAHCl solution, at concentration below p.c.r. (=7x10$^{-6}$ M), it co-adsorbs with the double chain surfactant, enhancing the surface activity of the latter, thereby, lowering the p.c.r. This is evident from the fact that mica surface becomes neutralized at 5x10$^{-6}$ M DOAHCl in the presence of 10$^{-6}$ M octanol (Figure 2.5). When the DOAHCl concentration is above the p.c.r., octanol cannot co-adsorb on in the DOAH$^+$ monolayer, as the surface is fully covered by DOAH$^+$ ions. However if the octanol concentration is raised high enough, the adsorbability of DOAH$^+$ ions increases so much that a significant amount of the surfactants (possibly in the form of DOAH$^+$-octanol complexes) adsorb in the second layer (Figure 2.8d). This causes an increase in the repulsive force and a decrease in hydrophobic force, as shown in Figure 2.6.

It is possible to estimate quantitatively the chain packing density (no. of chains per nm$^2$, which is the inverse of the area occupied per terminal methyl group) in both DAHCl and DOAHCl monolayers using experimentally measured adsorbed layer thickness ($t$) values. The effective area occupied by each chain in the monolayer ($A_{eff}$) is related to $t$ via:

$$A_{eff} = \frac{v}{t}$$  \hspace{2cm} (9)
where \( v \) is the volume per hydrocarbon chain, which may be obtained from the following equation given by Tanford (25):

\[
v = (27.4 + 26.9 \, n) \times 10^{-3} \, \text{nm}^3
\]  

(10)

where \( n \) represents the number of hydrocarbon groups in a single chain. The reciprocal of \( A_{\text{eff}} \) gives the number of chains per \( \text{nm}^2 \) in the monolayer, \( N \). It may be mentioned here that maximum surface coverages by hydrocarbon chains should correspond to one hydrocarbon chain per 0.2 \( \text{nm}^2 \) of the surface. Therefore, the maximum number of chains that can be packed into 1 \( \text{nm}^2 \) of the surface, \( N_{\text{max}} = 0.2^{-1} = 5 \). The ratio between \( N \) and \( N_{\text{max}} \) may then indicate the fractional surface coverage by hydrocarbon chains, \( f \), which may be used to compare the chain packing densities in different monolayers.

Shown in Table 2.2 are the calculated values of \( A_{\text{eff}} \), \( N \), \( v \) and \( f \) for the different self-assembled monolayers formed with DAHCl and DOAHCl in the presence and absence of neutral surfactants. The \( t \) values listed in the table were obtained both from the present work and literature. Calculations were not carried out for the DAHCl-octanol mixed monolayer. This is because the chain lengths of the ionic (\( n=12 \)) and neutral (\( n=8 \)) surfactants in the monolayer are different; hence, it is not clear as to which of the two \( n \) values the experimentally measured \( t \) value should correspond. For the DAHCl-dodecanol mixed monolayer, the \( t \) value reported in literature was used for the calculation.

The last column in Table 2.2 shows the \( D_2 \) values of the experimentally measured hydrophobic forces. As shown, \( D_2 \) increases with increasing \( f \). One exception is the DAHCl-Dodecanol system. Nevertheless, there seems to be a strong correlation between \( D_2 \) and the packing density of hydrocarbon chains at the surface. Note, in particular, the large difference in the \( f \) values between the DAHCl monolayer and the rest, which may explain why the hydrophobic forces measured between the monolayers of the former are short-ranged. Also, from the \( f \) values given in the table, one can see that a fractional surface coverage of approximately 0.7 is necessary for the onset of medium-ranged hydrophobic forces.
### TABLE 4.2

Calculation of chain packing density for various monolayers

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Concentrations (M)</th>
<th>( t ) (nm)</th>
<th>( v ) ((10^3 \text{ nm}^3))</th>
<th>( A_{\text{eff}} ) (nm²)</th>
<th>( N ) (nm⁻²)</th>
<th>( f )</th>
<th>( D_o ) or ( D_2 ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAHCl</td>
<td>(10^{-5})</td>
<td>0.5</td>
<td>350.2</td>
<td>0.7</td>
<td>1.43</td>
<td>0.29</td>
<td>1.4</td>
</tr>
<tr>
<td>DOAHCl</td>
<td>(7 \times 10^{-6})</td>
<td>0.9</td>
<td>242.6</td>
<td>0.27</td>
<td>3.7</td>
<td>0.74</td>
<td>5.2</td>
</tr>
<tr>
<td>DOAHCl + Oc⁺</td>
<td>(5 \times 10^{-6}+10^{-6})</td>
<td>1.0</td>
<td>242.6</td>
<td>0.24</td>
<td>4.17</td>
<td>0.83</td>
<td>6.2</td>
</tr>
<tr>
<td>DAHCl + Oc⁺</td>
<td>(5 \times 10^{-6}+5 \times 10^{-7})</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.8</td>
</tr>
<tr>
<td>DAHCl + Do⁺</td>
<td>(5 \times 10^{-6}+5 \times 10^{-7})</td>
<td>1.1</td>
<td>350.2</td>
<td>0.318</td>
<td>3.14</td>
<td>0.63</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Oc: Octanol; Do: Dodecanol
Figure 2.9 shows the decay lengths ($D_0$’s and $D_2$’s) of the hydrophobic forces plotted against the $\theta_a$ of the surfaces with which force measurements were conducted. In addition to the data obtained in the present communication, the figure also contains the data obtained by other investigators. As mentioned earlier, it can be seen from that the hydrophobic force changes sharply at $\theta_a \sim 90^\circ$. The present data obtained with DOAHCl alone and in the presence of octanol lie in the transition region where medium-range hydrophobic forces begin to emerge. Other data points in this regime include those obtained by Yoon and Ravishankar (7,14,15) with DAHCl in the presence of neutral surfactant molecules. It is very likely that the increase in $D_2$ at $\theta_a \sim 90^\circ$ is due to the sharp change in $f$ in these monolayers. At $\theta_a > 90^\circ$, it is possible that $f$ is even higher, maybe in the range of 0.9-1.0, which may explain why hydrophobic forces between such surfaces become long-ranged.

Some investigators suggested, on the other hand, that the sharp increase in hydrophobic forces observed at $\theta_a > 90^\circ$ may be attributed to the capillary forces associated with cavitation (26). Thermodynamically, the wetting tension becomes less than zero at $\theta > 90^\circ$, i.e.,

$$\gamma_{SV} - \gamma_{SL} < 0$$

(11)

where $\gamma_{SV}$ is the interfacial tension at the solid/vapor interface and $\gamma_{SL}$ is the same at the solid/liquid interface. Eq. [8] suggests that the free energy of a system decreases when a solid/liquid interface is replaced by the solid/vapor interface, i.e. cavitation should occur spontaneously at $\theta > 90^\circ$. For this reason, many researchers believe that the long-range hydrophobic forces observed at $\theta_a > 90^\circ$ are due to cavitation. Christenson and Claesson (26) observed the presence of vapor cavities when two hydrocarbon and fluorocarbon surfaces approach each other. Yuschenko et al. (27) showed that in the presence of macroscopic cavities, the attractive forces between hydrophobic forces are much larger than the van der Waals forces. However, the medium-range hydrophobic forces observed in the present work is not likely to be due to this mechanism since cavitation was not observed between two mica surfaces coated with DOAH$^+$ monolayers either in the presence or absence of octanol.
Figure 2.9. Decay length ($D_\alpha$, $D_2$) vs advancing contact angle ($\theta_a$) plot for data obtained with (i) mica surfaces in aqueous solutions of DOAHCl in the presence and absence of octanol (filled squares) (ii) literature data (open squares)
2.5 Conclusions

The results obtained in the present communication show evidence for a correlation between hydrophobic force and the hydrocarbon chain packing density on a surface. Calculations carried out here suggest that low packing density may indeed be the reason why monolayers of the primary amine, DAHCl, exhibit only short-ranged hydrophobic forces. If the packing density within these monolayers can be increased by some means, the hydrophobic interaction between them may also become stronger. Yoon and Ravishankar achieved this by incorporating neutral molecules like alcohols in between adsorbed DAH⁺ ions on the mica surface. In the present work, on the other hand, the higher packing density and, hence, the stronger hydrophobic forces have been achieved by using a double-chain secondary amine, DOAHCl. DOAH⁺ ions are able to form close-packed monolayers on the mica surface because the area per surfactant molecule is ~0.4 nm², which corresponds very well with the area per charge site on the mica surface.
2.6 References