

QUT Digital Repository:
<http://eprints.qut.edu.au/>



This is the author version published as:

Frost, Ray L. and Zbik, Marek (2010) *AFM study of forces between silicon oil and hydrophobic - hydrophylic surfaces in aqueous solutions*. Journal of Colloid and Interface Science, 349(2). pp. 492-497.

Copyright 2010 Elsevier

1
2
3 **AFM study of forces between silicon oil and hydrophobic - hydrophylic surfaces in**
4 **aqueous solutions**

5
6
7 **Marek S. Żbik and Ray L. Frost ***
8

9 **Faculty of Sciences, Queensland University of Technology 2 George Street, GPO Box 2434,**
10 **Brisbane Qld 4001 Australia.**
11
12
13

14 **Abstract**

15 An investigation has been made of the interactions between silicone oil and various solid
16 substrates immersed in aqueous solutions. Measurements were made using an atomic force
17 microscope (AFM) using the colloid-probe method. The silicone oil drop is simulated by
18 coating a small silica sphere with the oil, and measuring the force as this coated sphere is
19 brought close to contact with a flat solid surface. It is found that the silicone oil surface is
20 negatively charged, which causes a double-layer repulsion between the oil drop and another
21 negatively charged surface such as mica. With hydrophilic solids, this repulsion is strong
22 enough to prevent attachment of the drop to the solid. However, with hydrophobic surfaces
23 there is an additional attractive force which overcomes the double-layer repulsion, and the
24 silicone oil drop attaches to the solid. A "ramp" force appears in some, but not all, of the data
25 sets. There is circumstantial evidence that this force results from compression of the silicone
26 oil film coated on the glass sphere.

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)

27

28 **Keywords:** Silicon oil, interface forces, surface potential, AFM forces, PDMS interface forces.

29

30

31 **1. Introduction**

32

33 Paraffin surface is hydrophobic and frequently used as water repellent. In some investigation such
34 surface, when flat and smooth can be used as a model to study forces (using atomic force microscopy,
35 AFM) acting between hydrophobic surface and probe in aqueous solutions of different electrolytes and
36 surfactants. In this paper the AFM study was undertaken to measure forces between hydrophobic surface
37 and silicon oil (PDMS) which knowledge is important in all range of cosmetic products in beauty
38 industries.

39

40 Our earlier study [1] was focused on experimental development and preparation of suitable
41 hydrophobic surface for AFM force measurements. As a result the flat and smooth paraffin wax surface
42 which has been formed under the salt crystal was chosen as the hydrophobic substrate to force
43 measurements [1]. Comparative measurements were also conducted on the mica and Teflon surface.

44 The next main objective was to find a means of immobilizing a drop of silicone oil on a solid
45 substrate in the atomic force microscope (AFM), and pressing a “colloidal probe” – a silica sphere glued
46 to the AFM cantilever – against the drop.

47

48 To be successful, this method would require identification of a substrate material that would have a
49 finite contact angle of silicone oil when immersed in water. Silicone oil is well known to be an excellent
50 wetting agent for most materials. However, it was found that a mica surface would meet this requirement,
51 so long as the mica was first wet by water. A silicone drop placed on mica under water does not

52 completed wet the mica (as it does on dry mica); instead it forms a finite contact angle, albeit only about
53 15°. It should then be possible to use a system like that developed previously by Fielden and others [2,3]
54 for immobilizing air bubbles for AFM studies, whereby a hole is drilled through a sheet of mica atop a
55 hydrophobic material such as Teflon or polypropylene. The air bubble, or in this case the silicone oil drop,
56 would be attached to the hydrophobic material and would not spread past the edges of the hole in the
57 mica.

58

59 Unfortunately, in our attempts to implement this method for silicone oil, it was found that an oil film
60 formed between the Teflon and mica sheets. Then, during approach of the probe to the surface in the AFM
61 experiment, pressure on the mica sheet increased and oil was squeezed out of the gap, causing it to spread
62 past the edges of the hole and along the mica sheet.

63

64 Another difficulty in force measurements between surface and rather low viscosity silicon oil is very
65 hard to locate the small silicone drop and position the colloidal probe directly over it. In part this is due to
66 the low refractive index difference between silicone and water leading to low optical contrast and
67 visibility of the drop under water, and in part it is due to the mechanical arrangement of the AFM.
68 Alternatively, other methods of localizing a silicone oil drop could be investigated. Gillies at al [4]
69 investigated highly cross-linked PDMS droplets using colloidal probe in image mode then the in-build
70 software was used to centre the PDMS droplet directly beneath the colloid probe. PDMS droplets in this
71 experiment were highly elastic with Young's moduli in the range 10^6 Nm^{-2} .

72

73 In our case, with silicon oil with relatively low viscosity, a different method was tried. This consisted
74 of touching a very small quantity of silicone oil directly to the colloidal probe, forming a thin film of
75 silicone over the silica sphere, and then bringing the probe into contact with a flat solid surface. This has
76 the significant benefit of avoiding all alignment problems. Furthermore, it is very simple method. The

77 main drawbacks are (a) it will be important to know how thick the silicone film is, to allow proper
78 analysis of the data, and (b) the deformation of the silicone film will not be the same as the deformation
79 of a silicone drop, which will play a role in future studies of approach speed, viscosity and drop size.
80 However, if one thinks about it, the second drawback would be true of any system that – of necessity –
81 holds a partial drop of fluid (or air bubble) immobile in order to measure the forces that act on it.

82

83 **2. Experimental details**

84

85 A Nanoscope III AFM (Digital Instruments) was used in the force mode with scan head E. A standard
86 fluid cell and a scan rate of 0.1 and 1 Hz were used for all measurements. AFM cantilevers were
87 triangular, tipless, silicon nitride. The spring constant was nominal 0.12 N/m. Colloid probes were
88 prepared by attaching a particle to the end of cantilever. This was achieved using an optical microscope
89 (Olympus BH-2), with a micromanipulator attached to the stage. A heated stage was used for the gluing
90 process, as the resin used (Shell Epikote 1004) had a melting point of 100 °C. A tungsten wire electro –
91 sharpened was attached to the end of the cantilever. This wire was used to collect and to transport a glass
92 sphere of diameter 20-50 μm to a cantilever and place it on the resin at the top end of the cantilever. The
93 particle was sized after being mounted, using a CCD camera attached to the microscope's trinocular head,
94 a frame grabber, and an image analyzer (Galai, Cue 3 Israel). The image acquired could be magnified to
95 allow precise sizing ($\pm 5\%$) of the particles.

96

97 Paraffin wax commercially available was studied. X-ray diffraction pattern (described in [1]) of used
98 paraffin wax is shown to belong to orthorhombic space groups $Bb2_1m$.

99

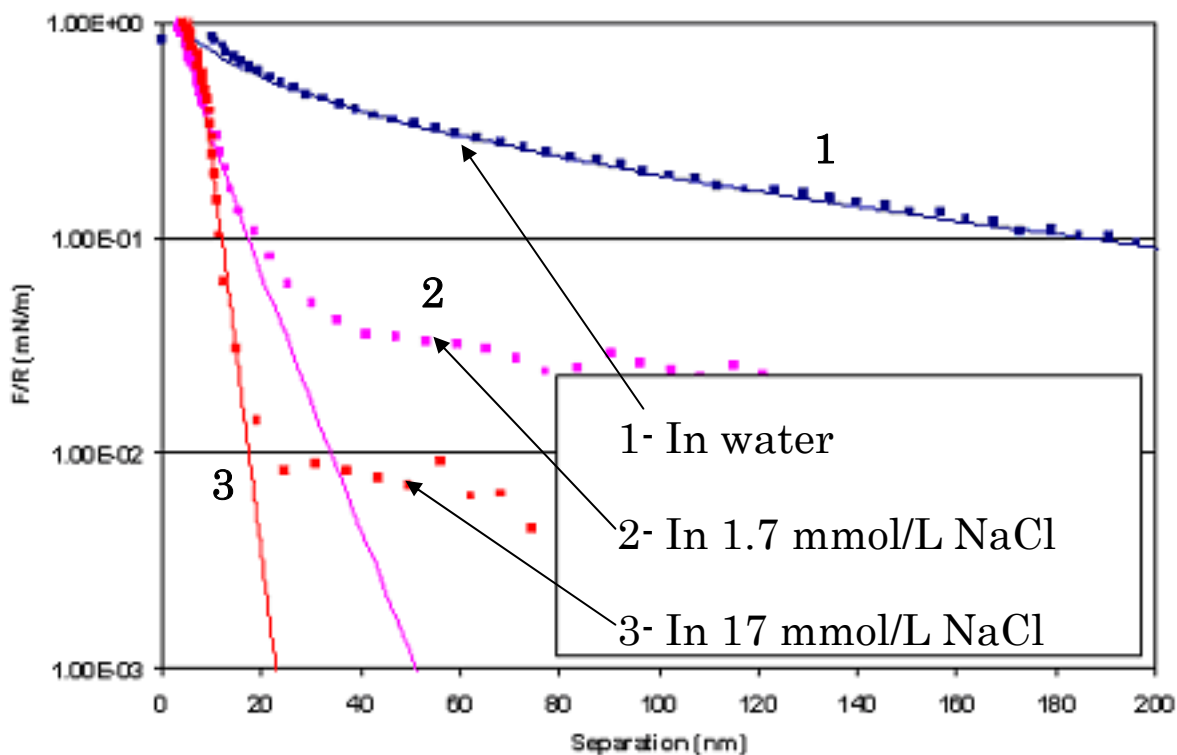
100 Wax was placed on top of the stainless still token (have to be hold on top of the AFM head by its
101 magnetic force) of diameter around 10 mm in few different ways. The simplest way is to melt small

102 fragment of paraffin and let it quench slowly on air. Other ways involved melting paraffin and quenched it
103 against smooth surface of mica, silicon wafer, salt crystal and polymer. Most of these surfaces inflicted
104 significant stress on paraffin when detached them except the salt crystal. Salt crystal from Sigma –
105 Aldrich as an IR crystal window unpolished, 11 x 30 x 7 mm was cleaved and atomically smooth was
106 placed on top of molten wax, than allowed to quenched slowly in room temperature and was subsequently
107 removed by dissolution in water.

109 **3. Results and discussion**

111 *Silicon wafer substrate in aqueous NaCl solution.*

112 AFM surface force measurements have been made for three combinations of probe/substrate, each at
113 three different salt concentrations. The results are shown in Figure 1-2, in which the measured force F
114 (normalised by the spherical probe's radius of curvature R) is plotted on a logarithmic scale against the
115 minimum distance D from the sphere's surface to the flat plate. This is the standard way to plot surface
116 force measurements, since the quantity F/R should be independent of the sphere's radius and so data from
117 different experiments can be compared. According to the Derjaguin approximation, F/R is 2π times the
118 interaction energy between two parallel flat plates at the same separation D , and this quantity can easily
119 be compared to theoretical calculations [5]. Positive values of F/R represent repulsion between the
120 surfaces.



121
 122 **Fig. 1** Forces measured between a silica sphere coated by a film of silicone oil of viscosity 60,000 cS,
 123 and a flat mica substrate, 1- in water, 2 in 1.7 mmol/L NaCl, 3 in 17 mmol/L NaCl. Theoretical curve was
 124 fitted in to the samples.

125
 126 Figure 1 shows results of measurements of forces between a 30 μm silica sphere coated by a film of
 127 silicone oil of viscosity 60,000 cS, and a flat mica substrate. The thickness of the film was not measured.
 128 Only the approach curves are shown, measured when the oil-coated sphere is pushed towards the
 129 substrate. What the data show is (a) there is a long-range repulsion between these two surfaces; (b) the
 130 decay of the force is quasi-exponential; (c) the decay length decreases as salt concentration increases; and
 131 (d) there is no adhesion between these surfaces (when adhesion is present, the force becomes negative in
 132 the “separation” curve, and typically there is an abrupt jump out from a small value of D to a large one).
 133 These results are entirely consistent with previous force measurements between silica and mica [6]. The
 134 repulsive force is explained by an electrical double-layer repulsion between surfaces which become
 135 charged on immersion in water, which leads to a quasi-exponential force whose range decreases with

136 electrolyte concentration [5, 7]. Theoretically, a van der Waals attraction is expected at small separations,
137 but this is not usually observed between silica and mica, probably due to the presence of a short-range
138 hydration repulsion [7]. Results indicate that, like the mica, the silicone oil/water interface must be
139 negatively charged.

140
141 The curves measured on separation are not included in this Figure, because there were complications
142 due to hydrodynamic effects. However, qualitatively one can say that no adhesion was observed, i.e. the
143 silicone oil drop did not attach to the mica substrate in the presence of salt. On some occasions it did
144 attach in water, but this effect was inconsistent.

145
146 Theoretical curves are included in the Figure 1. In the theoretical fits shown in the above figures, there
147 are three adjustable parameters – the surface potentials of the two surfaces, and the decay length of the
148 exponential. The decay length (Debye length) should be fixed by the known electrolyte concentration of
149 the two salt concentrations; however for the “pure” Milli-Q water the exact salt concentration is not
150 known (it must always be at least 10^{-7} mol/L from the self-dissociation of water, and is usually more than
151 2×10^{-6} mol/L from dissolved CO_2). Typically the background electrolyte level is somewhere around 10^{-5}
152 mol/L. Best fits to the “pure water” data were obtained using 3.5×10^{-6} mol/L in Figures 1 and 2.

153
154 The curve in Figure 1 is well fitted by surface potentials of -105 mV on both the surfaces. It would be
155 possible to obtain a similar fit to the data using other combinations such as -100 and -120 mV for the two
156 surfaces, so this experiment does not pin down the value for the silicone oil surface precisely. But since
157 -105 mV is a more reasonable value for mica, it is possible to conclude that the surface potential of silicone
158 oil in water is also in the neighborhood of -100 mV.

160 The surface potentials appear to fall significantly when salt is added, to about -30 mV according to the fits
161 to the other two curves in Figure 1. The correct Debye lengths, corresponding to the specified NaCl
162 concentrations, were used for these two curves. However, there is some uncertainty about these two data
163 sets due to possible hydrodynamic effects alluded to earlier. In particular, the curve for 17 mmol/L NaCl
164 showed some short-range “softness” which required a 4 nm offset of the theoretical curve. This may be due
165 to the hydrodynamic effects. Note also that the thickness of the silicone oil film on the sphere has not yet
166 been determined, and it is possible that this may result in a larger value of R and hence a re-scaling of F/R ,
167 which would result in different surface potentials to fit the data. Curves with salt present have “tails” that lie
168 well off the theoretical curves. This is most likely experimental error that is commonly encountered when
169 the forces are weak – there is usually significant scatter when $F/R < 10^{-2}$ mN/m.

170
171 The Fig. 2 shows forces measured between a silicone oil-coated sphere and a flat Teflon substrate.
172 Only approach curves are shown, because in every case there was adhesion observed on separation, that is,
173 the oil attached to the Teflon when the surfaces were close enough, forming a liquid bridge which must be
174 ruptured before the surfaces can be separated.

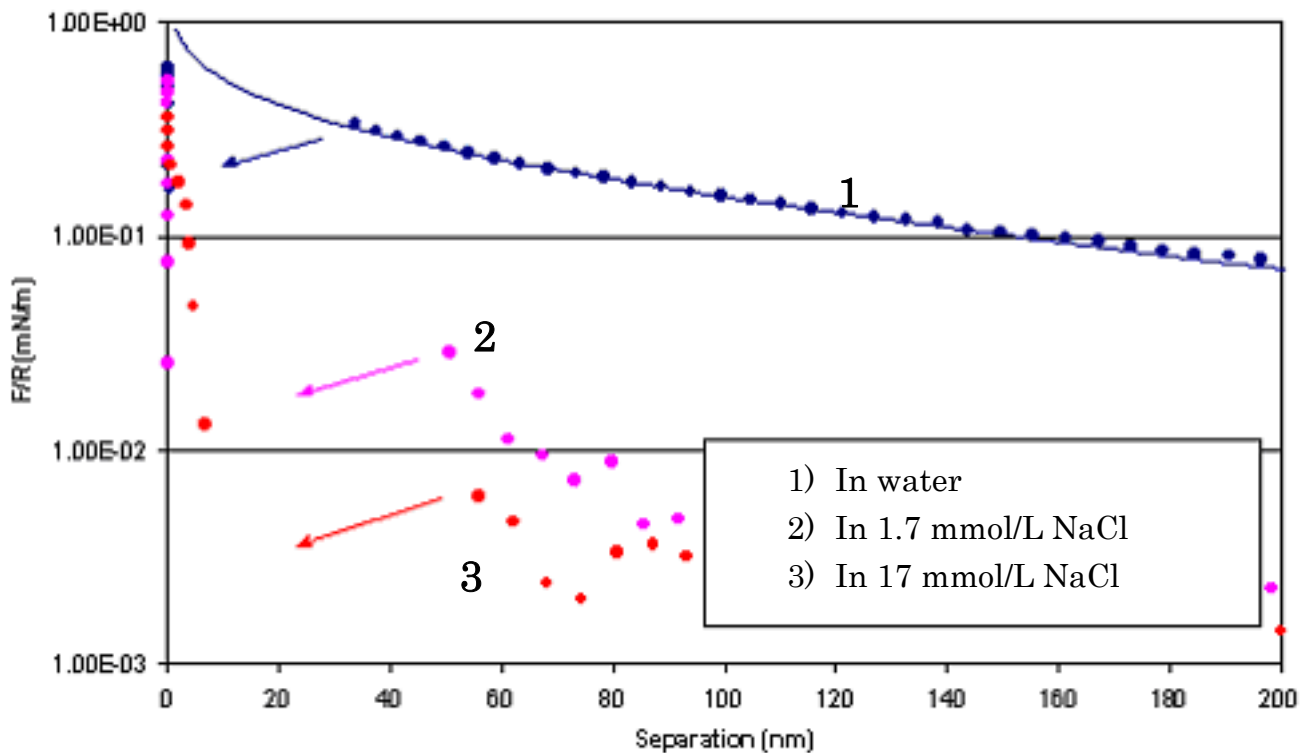


Fig. 2 Forces measured between a silicone oil-coated sphere and a flat Teflon substrate, 1- in water, 2 in 1.7 mmol/L NaCl, 3 in 17 mmol/L NaCl. Theoretical curve was fitted in to the sample studied in water.

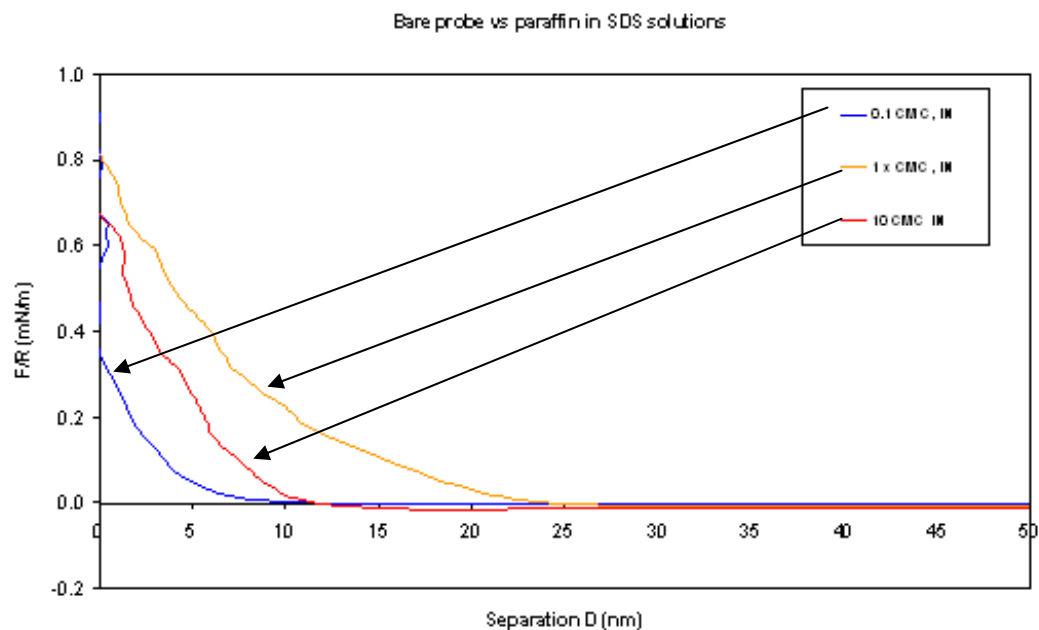
The forces on approach to Teflon again show a long-range repulsion, consistent with a negative surface charge on Teflon, but there is a significant new feature in these curves. They all show a jump into contact from a comparatively large distance – about 35 nm in water, 50 nm in 1.7 mmol/L NaCl, and 55 nm in 17 mmol/L NaCl. The jump cannot be accounted for by van der Waals attraction. This is a feature that has previously been observed between hydrophobic surfaces, and attributed to the presence of tiny air bubbles attached to the hydrophobic (and probably slightly rough) surface [9, 10]. There is a weak double-layer repulsion measured as the second surface (silicone oil) approaches the hydrophobic surface that is thought to be decorated with air bubbles, but as soon as an air bubble is contacted, a gaseous bridge forms between the surfaces and pulls them rapidly together. In the present system, it is not clear whether

189 the surfaces are bridged by air, by silicone oil, or both. There is also the possibility that in this experiment
190 it is not air bubbles, but residual drops of silicone oil attached to the Teflon, that cause the jump to contact.
191 What is clear is that once it is brought to within a few tens of nanometres, the silicone oil-coated sphere
192 becomes attached to the hydrophobic substrate. With the Teflon surface (Figure 2), a very good fit to the
193 water curve using the same surface potential of -105 mV for the silicone, and a value of -70 mV for the
194 Teflon. Weak double-layer repulsions are present in the two NaCl curves, but there is little point in fitting
195 these theoretically due first to the paucity of data points, and second to the additional uncertainty of not
196 knowing exactly where the plane of surface charge is, if it is situated at the surface of attached air bubbles
197 [10].

198 *Paraffin surface in SDS solutions*

199 The force measurements of oiled glass sphere against paraffin surface have been conducted in solutions
200 of the anionic surfactant, sodium dodecylsulphate (SDS) at $1/10^{\text{th}}$ of its CMC (i.e. 0.8 mM), at its CMC (8
201 mM) and 10 times the CMC (80 mM), against a paraffin surface.

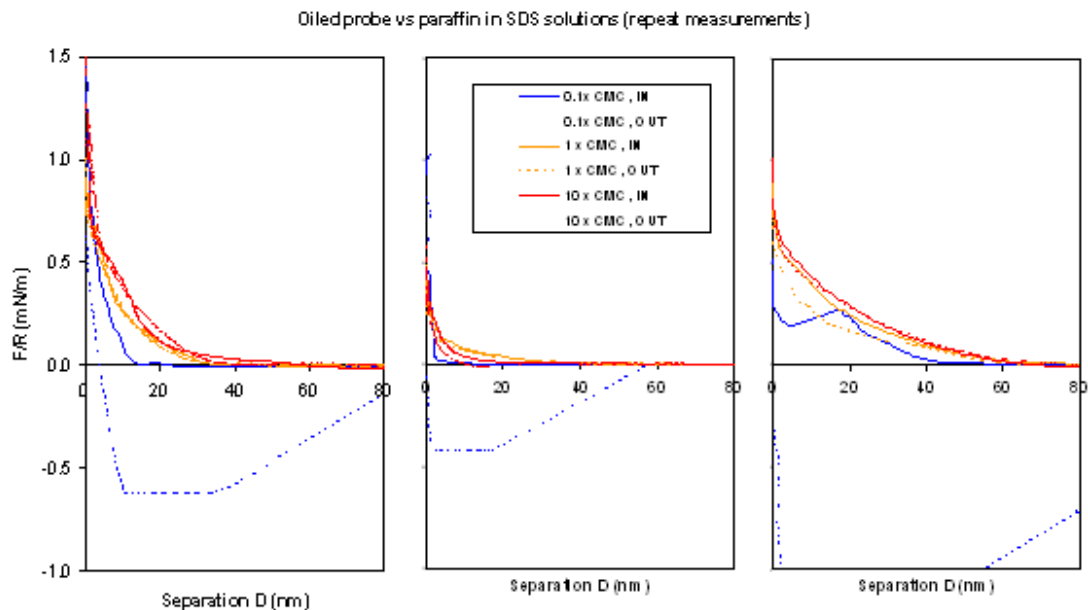
202 The first measurements, presented in Figure 3, were made with a bare glass probe against a paraffin
203 surface, i.e. in the absence of silicone oil. While the magnitude varied, the range and reversibility of the
204 force at all concentrations was consistent with electrical double-layer repulsion. For this to occur the
205 paraffin surface must be charged negatively by adsorption of SDS in a tails-down configuration, with
206 more adsorption occurring at and above the CMC. The force was reversible in all cases, meaning that no
207 adhesion is observed.



208
 209 **Fig 3.** AFM force measurements between a bare glass sphere and a flat paraffin surface in SDS
 210 solutions at three concentrations encompassing the CMC.

211
 212 At the CMC of SDS concentration curves showed a small jump into contact on approach and a
 213 distinct adhesion observed on separation, features which are not seen in Figure 3 but are consistent with
 214 other measurements using oil-coated probes against Teflon (Fig. 2) and paraffin (below).

215
 216 Figure 4 shows three series of repeat measurements in SDS with an oil-coated probe against a paraffin
 217 surface. In each case a medium-range repulsion is observed, and an adhesion is observed at $0.1 \times$ CMC
 218 but not at or above the CMC. The repulsion could be electrical double-layer below the CMC, but its range
 219 is too great to be attributed to double-layer force at or above the CMC.

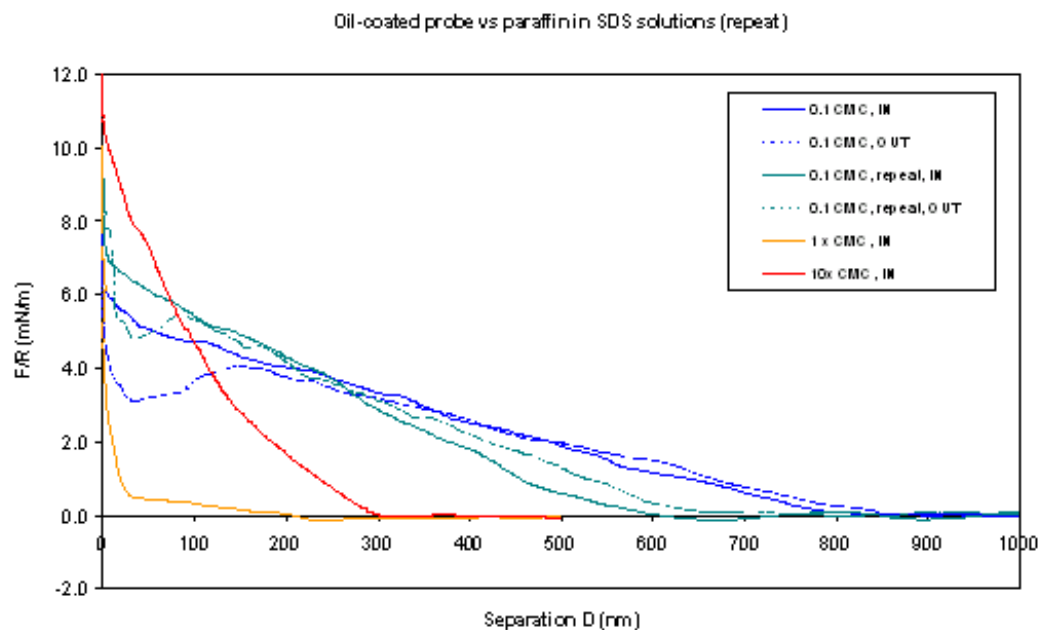


220

221 **Fig 4.** Three repeat measurements of forces between a silicone oil-coated glass sphere and a paraffin
 222 surface in SDS solutions at three concentrations.

223

224 Another repeat experiment was made in which a thicker film of silicone oil was intentionally applied
 225 to the glass sphere. This produced results with a different feature, shown in Figure 5. Now a long-range
 226 ramp is present at all concentrations. The ramp is longest in the first measurements made ($0.1 \times \text{CMC}$),
 227 decreases significantly in range and magnitude at $1 \times \text{CMC}$, and increases in magnitude at $10 \times \text{CMC}$. At
 228 and above the CMC the measured force is reversible on approach and separation, but at $0.1 \times \text{CMC}$ there
 229 is some irreversibility, indicating an adhesive component superimposed on the ramp. Indeed, aside from
 230 the presence of the ramp, there is qualitative resemblance between the results shown in Figures 4 and 5, if
 231 the forces shown in Figure 4 were superimposed on a linear ramp.

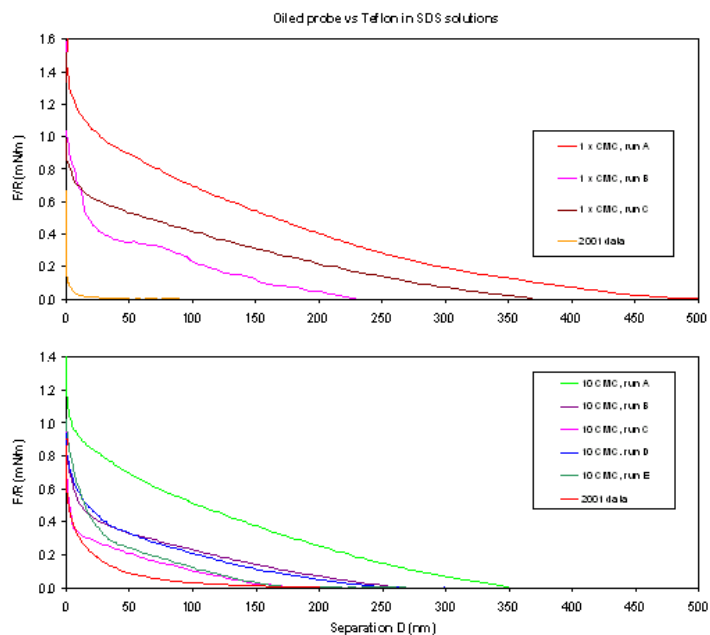


232

233 **Fig 5.** Another repeat measurement between an oil-coated sphere and flat paraffin surface. In this case
 234 the oil film was intentionally made thicker than in previous experiments.

235 ***Teflon surface in SDS solutions***

236 A repeat series of measurements was made of the force between an oil-coated sphere and a flat Teflon
 237 surface in SDS solutions at $1 \times$ and $10 \times$ the CMC, and the results are presented in Figure 6. Again a
 238 linear ramp is seen in all force curves. The slope and range of the ramp varies from measurement to
 239 measurement, but semi-quantitatively at least the forces look like a variable ramp plus a medium-range
 240 repulsion superimposed at $D < 20$ nm or so. All force curves are reversible, with no adhesion being
 241 detected.



242
 243 **Fig 6.** Several measurements of forces between an oil-coated glass sphere and a flat Teflon surface in
 244 SDS solutions at the CMC (top) and 10 times the CMC (below). For clarity only the approach curves are
 245 shown; the force was reversible (no adhesion) in all cases.

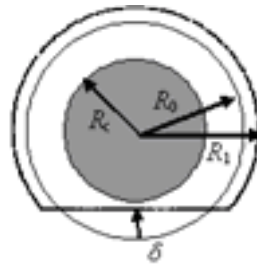
246
 247 The results against a paraffin surface that were presented in Fig. 4 appear do not fit a general picture
 248 of the forces between an oil-coated probe and hydrophobic surfaces in SDS solutions. That picture is that
 249 below the CMC there is a short-range repulsion, consistent with double-layer repulsion, and an adhesion;
 250 at the CMC the repulsion is of medium range, and above the CMC its range is longer still. In the latter
 251 two cases the force cannot be explained by double-layer repulsion, and is probably associated with build
 252 up of surfactant or surfactant/oil complexes at one or both surfaces.

253 As noted previously, a long -range, linearly -decaying repulsion that we have called a "ramp" force is
 254 observed in several of the experiments when an oil film is present. The fact that it has never been
 255 observed with a bare colloid probe is one indication that it may be the result of compressing the film.
 256 When observed, the range and magnitude of the ramp are usually found to decrease as the experiment
 257 proceeds, consistent with a dwindling amount of oil coating the probe.

258 It is very unusual that surface force decays linearly with distance. Also, the force is reversible in
 259 many cases, that is, it is not dissipative so it cannot be related to fluid viscosity. The only feature of an
 260 incompressible Newtonian oil film that could store energy when the film is deformed and release the
 261 energy when the deformation is removed is its surface tension.

262 The model presented below attributes the stored energy when deformation occurs to an increase in
 263 surface area and hence an increase in surface energy.

264 Consider the situation illustrated in Fig 6. A spherical drop of fluid originally has a radius R_0 . If the
 265 drop is flattened by an amount δ at one position, but maintains constant volume, then the radius of the
 266 remainder of the sphere must increase, let us say to R_1 . Note that the following argument holds also for a
 267 spherical shell, i.e., it is valid even if the core of the sphere is replaced by a solid of radius R_c , so long as
 268 $R_c < R_0 - \delta$. In other words, it is equally applicable to a fluid drop or to the present situation of a fluid film
 269 coating a solid sphere, where we assume that the flattening occurs by a repulsive interaction with an
 270 approaching flat surface.



271
 272 **Fig 7.** Dimensions involved in a model for deformation of a fluid drop, as discussed in the text.

273 The volume of a spherical cap of height δ is

274
$$V_\delta = \pi \left(R_0 \delta^2 - \frac{\delta^3}{3} \right) \quad , (1)$$

275 which for $\delta \ll R_0$ reduces to

276
$$V_\delta \approx \pi R_0 \delta^2 \quad . (2)$$

277 This is the volume of fluid that is taken from the original sphere and, assuming that the total fluid
 278 volume does not change, must be accommodated by a truncated sphere of larger radius R_1 . Again assuming

279 that $\delta \ll R_1$, to a first approximation the surface area of the expanded truncated sphere is given by the
 280 surface area of an expanded, non-truncated sphere. Our simple model assumes that the energy of the fluid
 281 drop is increased due to the expansion in its radius from R_0 to R_1 , neglecting corrections due to the
 282 truncation.

283 The increase in surface area A can be related to the "increase" in volume V of a sphere of radius R :

284
$$V = \frac{4}{3}\pi R^3 \quad ; \quad dV/dR = 4\pi R^2;$$

285 and
$$A = 4\pi R^2 \quad ; \quad \frac{\partial A}{\partial R} = 8\pi R \quad ;$$

286 from which

287
$$\frac{\partial A}{\partial V} = \frac{2}{R} \quad .(3)$$

288 Since the surface energy is

289
$$E_s = \gamma A \quad ,$$

290 where γ is the surface tension of the fluid (or more correctly, the interfacial energy between the fluid and
 291 its environment), we have

292
$$\frac{\partial E_s}{\partial V} = \frac{2\gamma}{R} \quad .(4)$$

293

294 The right-hand side of this equation can be recognized as the Laplace pressure in the fluid drop, so the
 295 equation has the familiar form for an energy change,

297
$$dU = PdV.$$

298

299 This is an expression for the change in surface energy associated with a change in volume of a sphere.
 300 Our argument is that the small volume "change" is the amount V_δ which inflated the radius of the fluid
 301 drop. The increase in energy is given by

$$\Delta E_s = \frac{2\gamma}{R} V_\delta = \frac{2\gamma}{R} \pi R \delta^2 = 2\pi\gamma\delta^2. \quad (5)$$

and the force associated with the energy change is given by its distance derivative

$$F = \frac{\partial E_s}{\partial \delta} = 4\pi\gamma\delta \quad (6)$$

Now, referring to Figure 7, the distance scale D of an AFM force measurement should be the distance between the horizontal flat surface and the surface of the solid core (which would give the point of constant compliance), which is related to the parameters indicated in the figure by

$$R_c + D + \delta = R_0$$

or

$$\begin{aligned} D &= R_0 - R_c - \delta \\ &= \delta_{\max} - \delta \end{aligned} \quad (7)$$

where δ_{\max} is the undeformed film thickness $R_0 - R_c$. Substituting for δ in the expression for force gives the final result:

$$\boxed{F = 4\pi\gamma(\delta_{\max} - D)} \quad (8)$$

This expression has the required form to match a ramp that decays linearly with D , declining from a positive (repulsive) value at $D = 0$ to zero at $D = \delta_{\max}$. The gradient of the ramp depends only on the interfacial tension γ , and it is interesting to note that the force is independent of the radius of the fluid drop. A small drop would have a higher Laplace pressure but this is compensated by a smaller flattened area for a given compression δ than would occur with a large drop, and the force = [pressure \times area] would be the same.

The distinctly linear ramps that have been observed in these measurements range in extent from 200 to 1600 nm, which are plausible values for the oil film thickness. This lends credence to the notion that the linear force ramp that has been observed in our investigations probably results from compressing the

326 silicone oil film. What then are the implications for interpreting the results when no such ramp is
327 observed? One possibility is that the film has been compressed down almost to zero thickness, but it is
328 still there and its surface chemistry still dictates the force that is measured. In this former case we might
329 expect to see similar forces measured (in the same solutions) with a supposedly oil-coated probe; in the
330 latter case the forces at short range should resemble the short-range part of the force when a ramp is
331 present. In several of the data sets presented (Figures 5 and 6) we have noted that the force looks like the
332 superposition of a ramp and a shorter-range force that was observed when there was no ramp, so the
333 results appear to be consistent with the continued presence of a very thin silicone film on the probe.

334 For these reasons we think it probable that even when a ramp is not present, the results obtained still
335 represent the interaction between a silicone oil surface and whichever other surface (e.g. paraffin or
336 Teflon) is present.

337 On the other hand, these ideas suggest a new opportunity that may now be available. If the above
338 model is correct, then measurements of the ramp's negative gradient give a direct determination of the
339 interfacial tension between the silicone (or other) oil drop and whatever solution conditions are being
340 investigated. If the interfacial tension falls to zero in a particular solution, then so does the ramp gradient:
341 the ramp would disappear and the force would indicate that no (thick) oil film is present. In fact that
342 would probably be correct, since zero interfacial tension would allow the oil to be emulsified by that
343 solution.

344 Results obtained from our multiple measurements (which were not been intent for this theory to test)
345 are rather variable due to imperfect linearity and reproducibility of the ramps, and as noted above they
346 suggest interfacial tensions ranging from 0.1 to about 10 mJ/m². At this stage we do not wish to place
347 great faith in the accuracy of these data, but it may be that the method can provide at least a useful pointer
348 to trends in interfacial energy if careful measurements of force ramps are pursued in the future.

350 3. CONCLUSIONS

351

352 This paper describes a method for making measurements of surface forces between silicone oil and
353 flat solid surfaces. The method is not what was originally envisaged, but there are good reasons for its
354 utility and continued use.

355 The initial experiments described here have produced clear qualitative information about the
356 interaction between silicone oil and hydrophilic (mica) and hydrophobic (Teflon and paraffin) surfaces in
357 water and NaCl salt solutions of 1.7 mmol/L and 17 mmol/L. Repulsive double-layer forces are measured
358 between all surfaces studied, which, since mica is known to be negative, demonstrates that the silicone oil
359 is also negatively charged in water. The repulsive force is strong enough to prevent attachment of silicone
360 oil to mica in salt solutions, but there is a hydrophobic attraction between silicone and Teflon which
361 results in attachment of the oil drop to this material.

362

363 The quantitative analysis of the data is difficult, probably due to difficulties with trace amounts of
364 surface-active contaminants and complex hydrodynamic effects. As an initial determination, the surface
365 potential of silicone oil in water is found to be -105 mV.

366

367 Several repeat measurements have been made in SDS solutions for paraffin and Teflon surfaces. In
368 general, the force between silicone oil and a hydrophobic substrate in SDS solutions below the CMC
369 shows a double-layer repulsion and an adhesive force in contact; at the CMC there is a medium-range
370 (some tens of nm) repulsion which is too long to be attributable to a double-layer force, and above the
371 CMC the range is usually increased further. This is suggestive of fluid structuring near one or both
372 surfaces due to formation of surfactant aggregates, possibly also involving the oil.

373

374 A "ramp" force appears in some, but not all, of the data sets. There is circumstantial evidence that this
375 force results from compression of the silicone oil film coated on the glass sphere. It remains unclear why

376 this effect is sometimes observed and sometimes not, and if this is the correct explanation, how the data
377 should be interpreted when the ramp is not there. There is some evidence to suggest that even when there
378 is no ramp, the probe remains coated by a very thin oil film that imparts its surface chemistry to the
379 probe.

380

381 A simple and plausible model has been developed that accounts for a repulsive force ramp that declines
382 linearly with separation. The model is based on the idea that when a spherical volume of immiscible fluid
383 is distorted by a repulsive interaction with a flat surface, its surface area and hence surface energy
384 increases as the distortion proceeds, which means that a repulsive force is present.

385

386 The model predicts that the ramp force is independent of the radius of the fluid sphere, and its gradient is
387 simply related to the interfacial tension. This provides, at least in principle, a new method of determining
388 the interfacial tension between immiscible fluids, such as silicone oil and surfactant/polymer solutions.

389

390

391 **Acknowledgements-** The author would like to acknowledge Prof. Roger Horn from Ian Wark Research
392 Institute, University of South Australia under whom inspiration, supervision and leadership this work was
393 conducted.

394

395

References

- [1] Zbik M. & Horn R. Colloids and Surfaces A, Special Issue, Electrokinetic Phenomena, Krakow 2002, Z.Adamczyk and M.Kosmulski, guest editors. 222, (2003) 323-328.
- [2] M.L. Fielden, R.A. Hayes, J. Ralston, Langmuir 12 (1996) 3721-3727.
- [3] H-J. Butt, Journal of Colloid and Interface Science 166 (1994) 109-117.
- [4] G. Gillies, C.A. Prestidge, P. Attard, Langmuir 18 (2002) 1674-1679
- [5] J. N. Israelachvili, Intermolecular and Surface Forces. 2nd ed. (1991) London, Academic Press.
- [6] W.A. Ducker, T.J. Senden, R.M. Pashley, Nature 353 (1991) 239-241.
- [7] R. J. Hunter, Foundations of Colloid Science. Vol.1, (1987) Oxford, Clarendon Press, Chapter 7.
- [8] R.G. Horn, D.T. Smith, W. Haller, Chem.Phys.Lett. 162 (1989) 404-408.
- [9] A. Carambassis, L.C. Jonker, P. Attard, M.W. Rutland, Phys.Rev.Lett. 80 (1998) 5357-5360.
- [10] R.F. Considine, R.A. Hayes, R.G. Horn, Langmuir 15 (1999) 1657-1659.
- [11] R.M. Pashley, J.Colloid Interface Sci. 83 (1981) 531-546.

412 **List of Figures**

413 Figure 1 Forces measured between a silica sphere coated by a film of silicone oil of viscosity 60,000 cS,
414 and a flat mica substrate, 1- in water, 2 in 1.7 mmol/L NaCl, 3 in 17 mmol/L NaCl. Theoretical
415 curve was fitted in to the samples.

416 Figure 2 Forces measured between a silicone oil-coated sphere and a flat Teflon substrate, 1- in water, 2
417 in 1.7 mmol/L NaCl, 3 in 17 mmol/L NaCl. Theoretical curve was fitted in to the sample studied
418 in water.

419 Figure 3 AFM force measurements between a bare glass sphere and a flat paraffin surface in SDS
420 solutions at three concentrations encompassing the CMC.

421 Figure 4 Three repeat measurements of forces between a silicone oil-coated glass sphere and a paraffin
422 surface in SDS solutions at three concentrations.

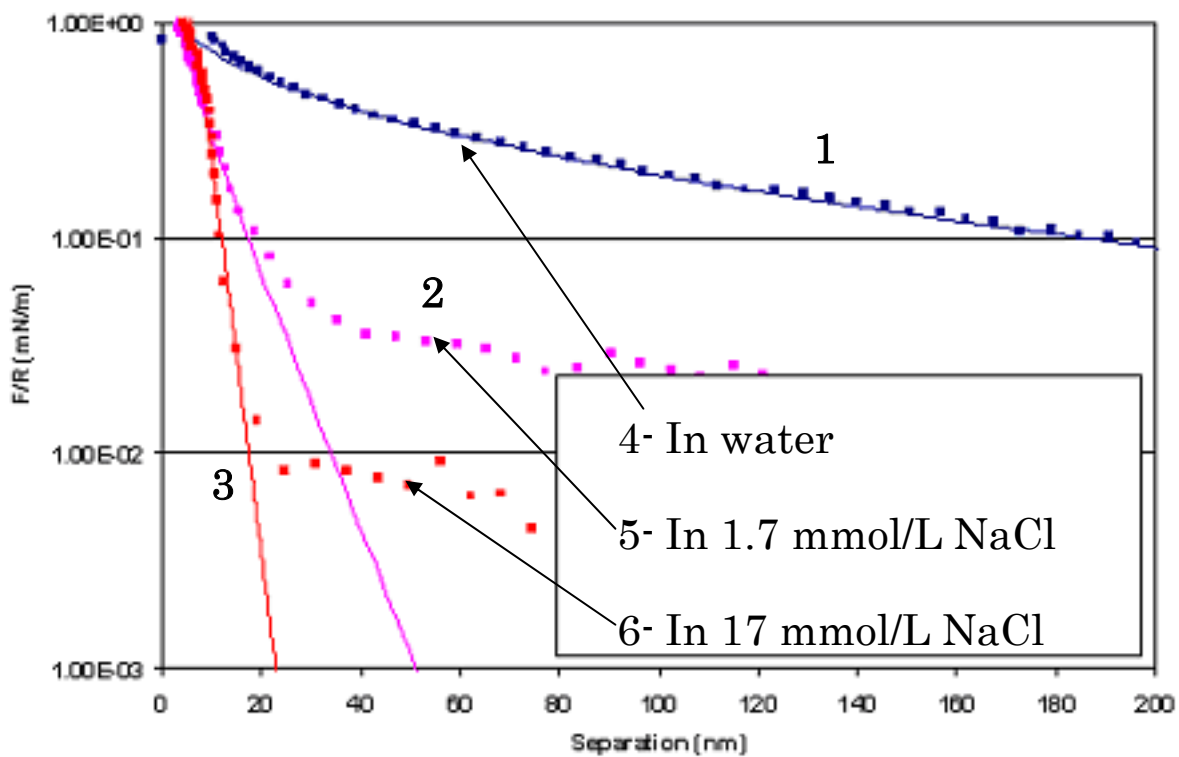
423 Figure 5 Another repeat measurement between an oil-coated sphere and flat paraffin surface. In this case
424 the oil film was intentionally made thicker than in previous experiments.

425 Figure 6 Several measurements of forces between an oil-coated glass sphere and a flat Teflon surface in
426 SDS solutions at the CMC (top) and 10 times the CMC (below). For clarity only the approach
427 curves are shown; the force was reversible (no adhesion) in all cases.

428 Figure 7 Dimensions involved in a model for deformation of a fluid drop, as discussed in the text.

429

430



431

432

433

434

435

436

437

438

439

440

441

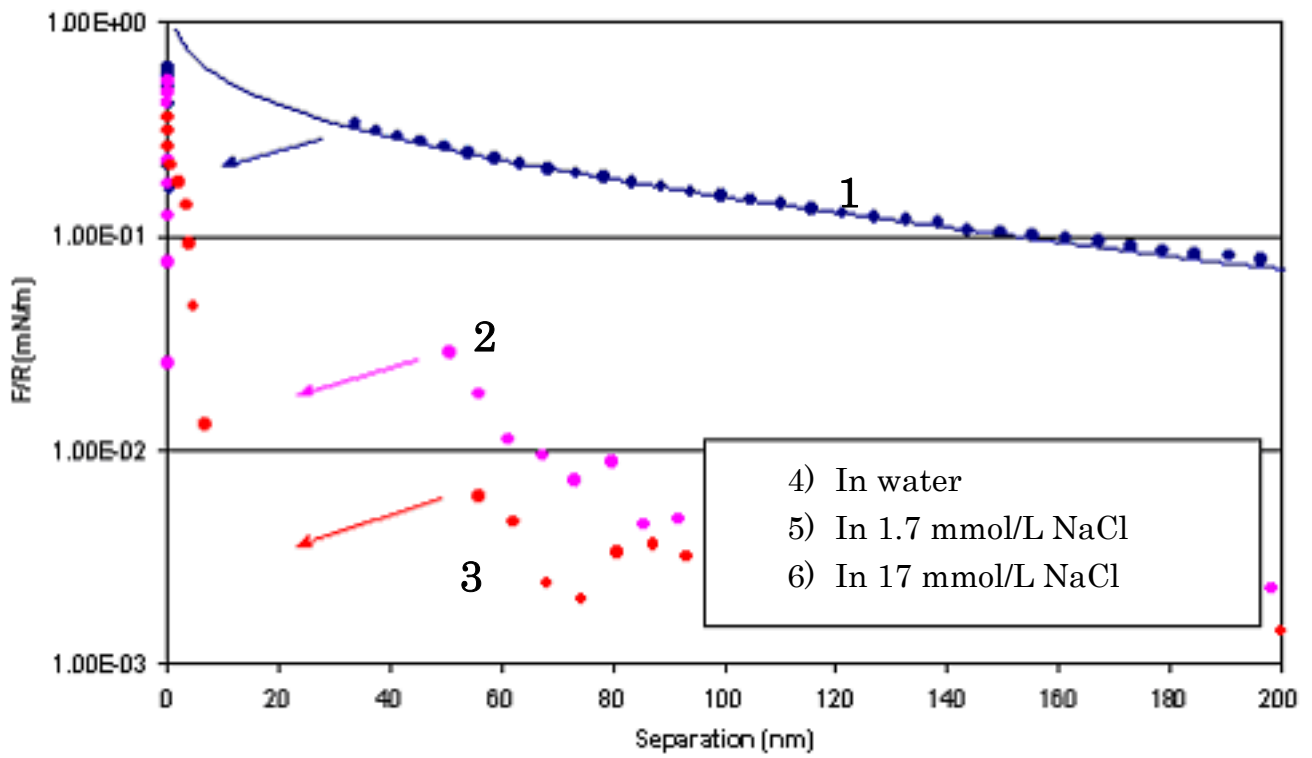
442

443

444

445

Fig. 1 Forces measured between a silica sphere coated by a film of silicone oil of viscosity $60,000\text{ cS}$, and a flat mica substrate, 1- in water, 2 in 1.7 mmol/L NaCl , 3 in 17 mmol/L NaCl . Theoretical curve was fitted in to the samples.



446

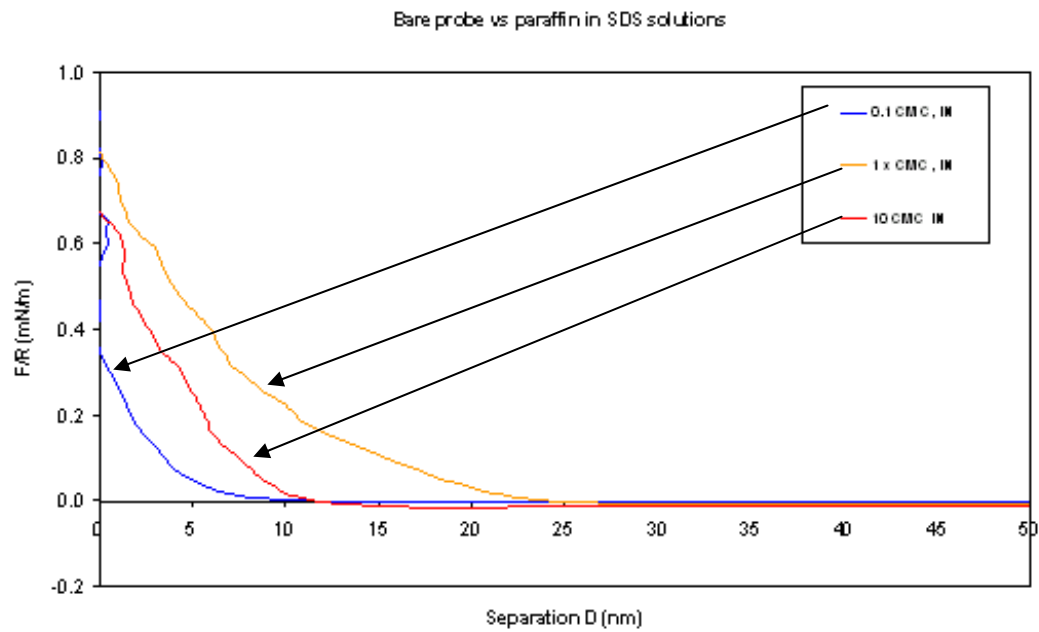
447

448

449

450

Fig. 2 Forces measured between a silicone oil-coated sphere and a flat Teflon substrate, 1- in water, 2 in 1.7 mmol/L NaCl, 3 in 17 mmol/L NaCl. Theoretical curve was fitted in to the sample studied in water.



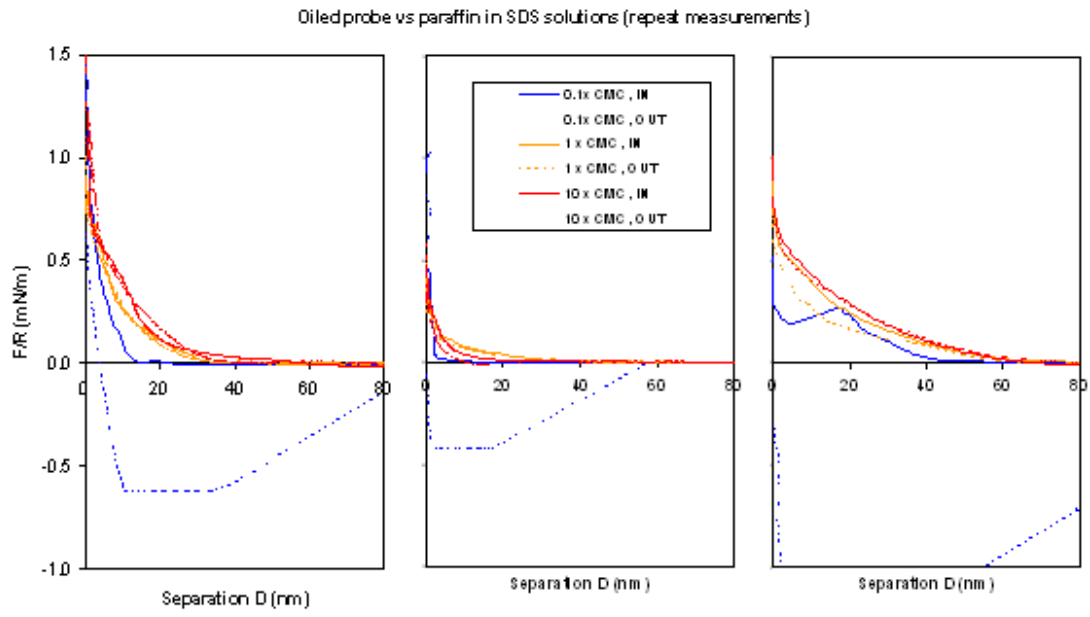
451

452 **Fig 3.** AFM force measurements between a bare glass sphere and a flat paraffin surface in SDS solutions

453 at three concentrations encompassing the CMC

454

455



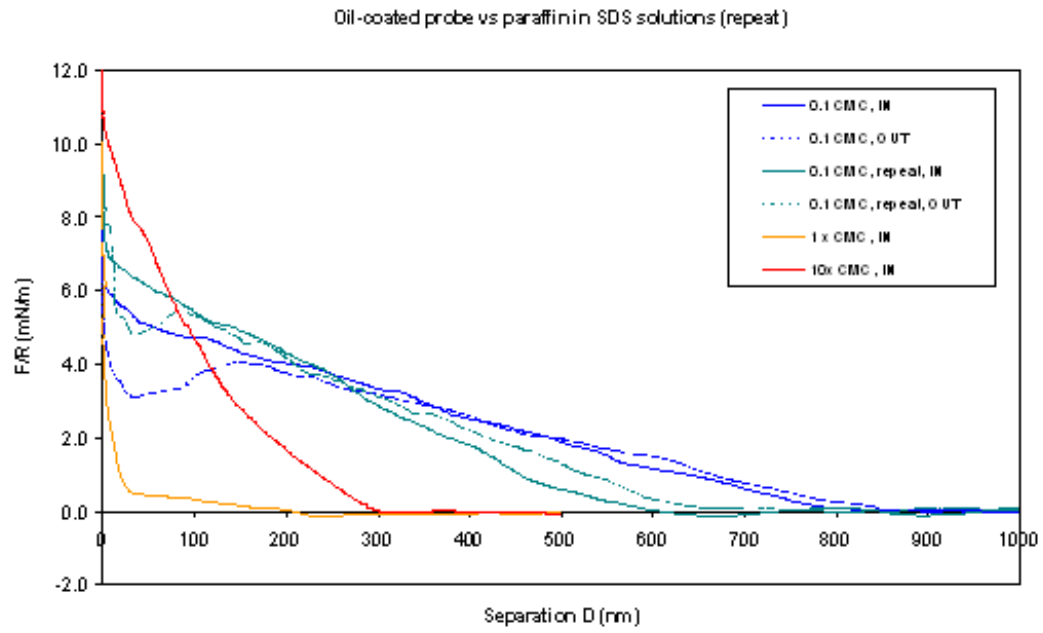
456

457

458

459

Fig 4. Three repeat measurements of forces between a silicone oil-coated glass sphere and a paraffin surface in SDS solutions at three concentrations.



460

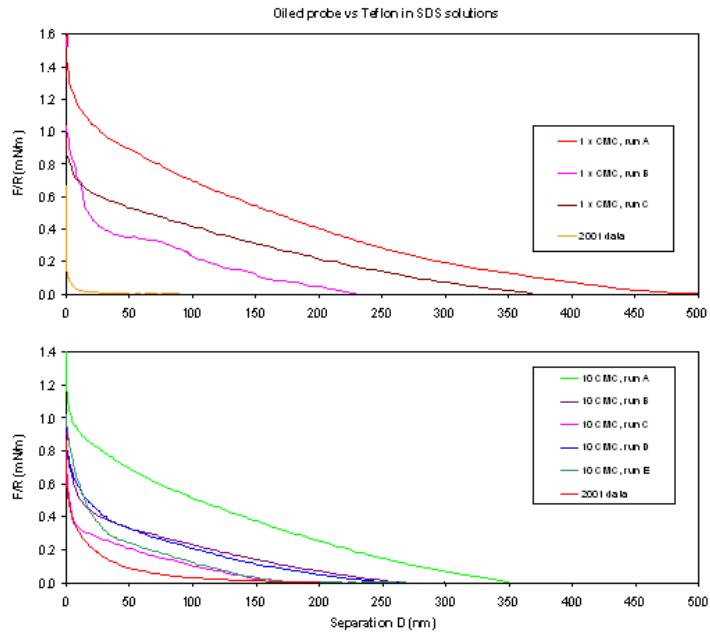
461

462

463

464

Fig 5. Another repeat measurement between an oil-coated sphere and flat paraffin surface. In this case the oil film was intentionally made thicker than in previous experiments.



465

466

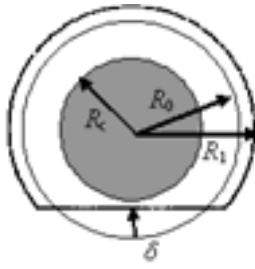
467

468

469

Fig 6. Several measurements of forces between an oil-coated glass sphere and a flat Teflon surface in SDS solutions at the CMC (top) and 10 times the CMC (below). For clarity only the approach curves are shown; the force was reversible (no adhesion) in all cases.

470



471

472 **Fig 7.** Dimensions involved in a model for deformation of a fluid drop, as discussed in the text.

473

474