Use of the Equilibrium Contact Angle as an Index of Contact Surface Cleanliness

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ABSTRACT

Advancing contact angles formed by water and aqueous ethanol solutions were measured on both bare surfaces and film-covered surfaces of acrylic, glass, hydrophilic and hydrophobic silicon, polycarbonate, polyester, and #304 stainless steel. Each bare surface was initially characterized with respect to its hydrophilic/hydrophobic balance. Both homogeneous protein films and heterogenous milk films were prepared on each surface; the adsorbed mass comprising each film was measured with ellipsometry. Contact angle methods proved useful in detecting the presence of a protein film on sufficiently hydrophilic or hydrophobic surfaces, i.e., materials for which \( W_{c}^{p} \) (the polar component of the energy required to separate water from its surface) is greater than 55 mJ/m\(^2\) or less than 37 mJ/m\(^2\). Contact angle methods were found to be useful for detecting the presence of a milk film on solid surfaces as well. However, the detection limits were dependent not only on \( W_{c}^{p} \) but also on the ethanol concentration of the diagnostic liquid used.

Currently, ellipsometric, spectroscopic and radiological methods can answer the question of material cleanliness, but they are too costly and too complex for routine use (11). Excessive time and money to train an operator might also be required. Microbiological, gravimetric and chemical methods are also available to detect contamination of food contact surfaces (1), but some are time consuming and may lack sensitivity to low contaminant coverage.

Contact angle methods have been used for decades to assist surface characterization. A number of workers have used contact angle techniques to detect surface contamination by hydrocarbons (14,16,17), and it was thought that contact angle methods could be used only to determine hydrophobic contamination on hydrophilic surfaces, i.e., contamination on those surfaces exhibiting a free energy greater than that of water, about 72 mJ/m\(^2\) (13). In this case, a drop of water would be expected to “bead” on a contaminated surface, and to completely spread on a bare surface.

The objectives of this study were to record contact angle data for different liquids on a variety of fouled and cleaned surfaces in order to establish the existence of a relationship between contact angle and mass of soil, and to define the limitations associated with use of the contact angle as an index of contact surface cleanliness. Simple, sessile drop contact angle methods were used to analyze both bare surfaces and film-covered surfaces. Both homogeneous protein films and complex, heterogenous milk films were prepared on various solid surfaces and studied.

Attempts to compare contact angle results from different laboratories have been largely unsuccessful, partially due to measurement under different experimental conditions and with different procedures. A major factor has been the difference in drop volumes used in different laboratories (7,9,14). Therefore, initial tests were carried out to determine the effect of drop volume on the equilibrium contact angle for combinations of solids and liquids of varying polar and nonpolar character. The results of the volume study, reported earlier (12), defined an appropriate drop volume for use in the remainder of this work.
MATERIALS AND METHODS

Solid material preparation

Six solid materials were used in this study: #304 stainless steel, glass (Eric Scientific Co., Portsmouth, NH), silicon (Wacker Siltronic Corp., Portland, OR), and three polymers (Sheffield Plastics, Inc., Sheffield, MA): acrylic, polycarbonate and polyester. All of the materials were cut into plates of approximately 2 x 2 cm. The surfaces of the three polymers were protected during shipment and storage with a protective film applied by the manufacturer. The #304 stainless steel was polished to a mirror finish.

Prior to use, each sample plate, with the exception of silicon, was cleaned with ultrasonic treatment for 10 min, rinsed with deionized water, and dried at room temperature in a desiccator. The silicon wafers were divided into two groups; one group was treated to be hydrophilic and the other treated to be hydrophobic according to Jonsson et al. (5). Hydrophilic silicon wafers were prepared as follows: (a) washed in a mixture of NH4OH:H2O2:H2O (1:1:5) at 80°C for 5 min; (b) rinsed with distilled water; (c) washed in HCl:H2O2:H2O (1:1:5) at 80°C for 5 min; (d) rinsed with distilled water; and (e) stored in a 50% ethanol solution until use. Hydrophobic silicon wafers were prepared as follows: (a) hydrophilic slides were treated for 10 min with 10% dichlorodimethylsilane in trichloroethylene; (b) rinsed in trichloroethylene, then acetone, and finally 100% ethanol; and (c) dried with dry nitrogen gas and stored in a desiccator until use.

The polar component of the energy required to separate water from each solid surface was determined according to methods detailed by McGuire (10); this polar energy component provides a measure of solid surface hydrophilicity. Basically, contact angle data were used to calculate the polar component of the work of adhesion (\(W_p, \text{mJ/m}^2\)) between each material under study and a drop of each of a series of diagnostic liquids placed on its surface. A plot of \(W_p\) against the corresponding polar component of diagnostic liquid surface tension (\(\gamma_\text{LV}^p, \text{mN/m}\)) was then constructed for each material. The resulting relationship was observed to be linear in all cases, i.e., \(W_p = k \gamma_\text{LV}^p + b\), where the slope, \(k\) (dimensionless) and intercept, \(b\) (mJ/m²) are specific to each solid surface. The value of the polar component of the work of adhesion between any given solid surface and water (\(W_p^w\) water) can be calculated according to \(W_p^w = k \gamma_\text{LV}^w + b\). Actual contact angle data for water therefore need not be used, avoiding potentially serious problems associated with using pure water as a diagnostic liquid (2).

Fouling and cleaning procedures

\(\beta\)-Lactoglobulin films. Two sample plates of each of the six solid materials were contacted with \(\beta\)-lactoglobulin in phosphate buffer (pH 7) at 40°C for 30 min with agitation. The concentration of \(\beta\)-lactoglobulin ranged from 100 to 3100 mg/L with 300 mg/L increments. The materials were subsequently rinsed with tap water for 20 s at room temperature, and then dried overnight in a desiccator. Buffer solutions were prepared as needed and used immediately.

Milk films. Each material with the exception of silicon was contacted with raw, whole milk (Miller’s Dairy, Harrisburg, OR) at 40°C for 30 min with agitation. All the materials were then rinsed with tap water for 10 s at room temperature, and dried overnight in a desiccator. Buffer solutions were prepared as needed and used immediately.

Each of the prepared milk films were divided into five groups; two samples of each material were placed in each group. Each group was cleaned by one of five different methods: (I) samples were immersed in tap water at 40°C for 10 min with agitation; (II) samples were immersed in a 25% H3PO4 (J.T. Baker Chemical Co., Phillipsbury, NJ) solution at 40°C for 10 min with agitation; (III) samples were immersed in an aqueous solution of monocarbamide dihydrogensulphate (MCDS) and a proprietary surfactant (Unocal Chemicals Division, Los Angeles, CA) at 40°C for 10 min with agitation (the cleaning solution was prepared such that the concentration of H2SO4 was 25% and that of surfactant was 5% by mass); (IV) a two-step process in which samples were contacted with a chlorinated alkaline cleaner (Cold-War™, Klenzade Division, Economics Laboratory, Inc., St. Paul, MN) for 5 min at 40°C with agitation, followed by a 10 s tap water rinse, and then immersed in an acid detergent (PL-3, Klenzade Division) for 5 min at 40°C with agitation (the alkaline cleaner was prepared at the rate of 1 oz : 3 gal of tap water (pH 11.83), and the acid detergent was prepared at the rate of 1 oz : 5 gal of tap water (pH 2.59) as recommended by the manufacturer); and (V) a two-step process in which the first alkaline cleaning step is the same as that used in (IV), followed by a 10 s tap water rinse, and immersion in MCDS (used at the rate of 1 oz : 20.7 gal tap water at an equivalent acidity (pH 2.59) with the PL-3 used above) for 5 min at 40°C with agitation.

Each single step cleaning method was followed by a 20 s rinse with tap water; the two-step cleaning methods were followed by a 10 s rinse with tap water.

Ellipsometry

Ellipsometry is an optical technique used to determine the thickness and refractive index of thin films. The ellipsometer measures changes in the state of polarization of light upon reflection from a film-covered surface. In brief, a laser beam of known physical properties is transmitted to a surface and reflected. Changes in the physical properties of the reflected beam are dependent on the properties of the film-covered surface; those changes are detected and transferred to a microcomputer. A computer program written in our laboratory converts this input into values of film thickness and refractive index. Absorbed mass can then be calculated with the values of thickness and refractive index according to the Lorentz-Lorenz relationship as experimentally validated by Cuypers et al. (4).

An automated ellipsometer (Model L104B, Gaertner Scientific Corp., Chicago, IL) was used in this study. The angle of incidence used was 70°, and the wavelength of light was 6328 Å. Substrate optical constants required for evaluation of film thickness and refractive index were measured for each material prior to film formation. The thickness and refractive index of the film-covered surfaces were recorded at approximately 20 different surface locations for each material. Absorbed mass was calculated from each data set of thickness and refractive index; the average of those values of adsorbed mass was recorded for each material.

Ellipsometry requires that sample plates be highly specular. Since the three polymers and glass are transparent, one side of each material was blackened evenly with spray paint to prevent reflection of the laser beam from the other side of the material during ellipsometric analysis.

Contact angle measurements on fouled and cleaned surfaces

Contact angle measurements were performed using a sessile drop contact angle goniometer equipped with an environmental chamber and a microsyringe assembly (NRL Model 100-00, Rame-Hart, Inc., Mountain Lakes, NJ). Solid materials were individually placed in the sample chamber, which was maintained at approximately 25°C under water-saturated conditions, and contacted with a liquid drop produced by the microsyringe. Advancing contact angles were measured at both sides of each drop. At least eight contact angle readings were recorded for each diagnostic liquid and solid surface combination.
The diagnostic liquids used in this study included deionized and distilled water, and aqueous solutions of ethanol (EM Science, Cherry Hill, NJ) prepared at 10, 20, 30, and 40 volume% concentrations. The drop volume used throughout the study was 20 μl, according to recommendations from work reported earlier (12).

RESULTS AND DISCUSSION

Solid surface characterization

Surface properties of each material related to their hydrophilic/hydrophobic balance were determined. A plot of $W^p$ vs. $\gamma^p_L$, constructed for each material, is shown in Fig. 1. The slope of each plot, k, and its ordinate intercept, b, were recorded. The parameters k, b, and $W^p_{\text{water}}$ are listed in Table 1. These results indicate that hydrophilic and hydrophobic silicons exhibit the most hydrophilic and hydrophobic surfaces, respectively. The remaining materials, listed in order of decreasing hydrophilicity, are glass, #304 stainless steel, acrylic, polyester, and polycarbonate.

Contact angles of aqueous ethanol solutions on β-lactoglobulin films

Solid surfaces were contacted with β-lactoglobulin solutions of varying concentration, yielding protein films of varying adsorbed mass. Contact angles and absorbed mass were recorded on both clean and film-covered surfaces, and a plot of contact angle vs. adsorbed mass was constructed for each material.

The change in contact angle upon film formation (i.e., the average value of $\theta$ evaluated for the film covered samples of a given surface minus $\theta$ evaluated for the bare surface) decreased with increasing solid surface hydrophobicity as shown in Table 2. Moreover, very hydrophobic and very hydrophilic materials exhibited a large change in contact angle upon film formation. A lesser change in contact angle was exhibited by materials of intermediate hydrophilicity. This would indicate that it is most appropriate to detect the presence of a protein film by contact angle methods on very hydrophilic or very hydrophobic materials.

Plots of the relationship between contact angle and adsorbed mass showed that for the hydrophilic surfaces (hydrophilic silicon, glass, and #304 stainless steel), contact angles exhibited an apparent step increase upon film formation, indicating an increased surface hydrophobicity. Another feature of these plots was that no clear change of contact angle with adsorbed mass was observed beyond the initial increase. It is consequently not possible to quantify the actual value of adsorbed mass with contact angle analysis. This was expected since the contact angle is influenced only by the outermost layers of contaminant (9,15).

In agreement with published observations of protein adsorption to hydrophilic surfaces (8), the dominant adsorption mechanism for β-lactoglobulin at these three surfaces is proposed to be electrostatic in nature; that is, some hydrophilic parts of β-lactoglobulin interact with the hydrophilic surface, possibly exposing hydrophobic regions to adsorb.

<table>
<thead>
<tr>
<th>Solid</th>
<th>k, dimensionless</th>
<th>b, mJ/m²</th>
<th>$W^p_{\text{water}}$, mJ/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrophilic silicon</td>
<td>1.99 (0.15)</td>
<td>-0.10 (4.8)</td>
<td>98.7</td>
</tr>
<tr>
<td>glass</td>
<td>1.95 (0.11)</td>
<td>-9.0 (3.6)</td>
<td>87.9</td>
</tr>
<tr>
<td>s. steel</td>
<td>1.77 (0.06)</td>
<td>-11 (2.1)</td>
<td>76.5</td>
</tr>
<tr>
<td>acrylic</td>
<td>0.98 (0.09)</td>
<td>-13 (2.9)</td>
<td>35.2</td>
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<tr>
<td>polyester</td>
<td>0.78 (0.09)</td>
<td>-15 (2.9)</td>
<td>23.5</td>
</tr>
<tr>
<td>polycarbonate</td>
<td>0.44 (0.22)</td>
<td>-10 (6.5)</td>
<td>12.0</td>
</tr>
<tr>
<td>hydrophobic silicon</td>
<td>0.06 (0.10)</td>
<td>9.4 (3.5)</td>
<td>12.4</td>
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</table>

<table>
<thead>
<tr>
<th>Solid</th>
<th>$\Delta$ Contact angle, °</th>
<th>20% EtOH</th>
<th>40% EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrophilic silicon</td>
<td>52.1 (6.70)</td>
<td>49.7 (6.43)</td>
<td>39.1 (7.80)</td>
</tr>
<tr>
<td>glass</td>
<td>38.0 (3.53)</td>
<td>29.5 (3.15)</td>
<td>24.9 (3.00)</td>
</tr>
<tr>
<td>s. steel</td>
<td>22.4 (3.47)</td>
<td>12.3 (2.67)</td>
<td>7.19 (3.16)</td>
</tr>
<tr>
<td>acrylic</td>
<td>-4.93 (1.42)</td>
<td>-7.69 (2.35)</td>
<td>-6.72 (2.00)</td>
</tr>
<tr>
<td>polyester</td>
<td>-15.2 (2.32)</td>
<td>-17.5 (2.26)</td>
<td>-15.2 (2.65)</td>
</tr>
<tr>
<td>polycarbonate</td>
<td>-27.6 (2.33)</td>
<td>-20.2 (2.69)</td>
<td>-17.2 (2.31)</td>
</tr>
<tr>
<td>hydrophobic silicon</td>
<td>-11.4 (8.04)</td>
<td>-10.6 (4.81)</td>
<td>-4.60 (2.36)</td>
</tr>
</tbody>
</table>
the surroundings during the drying step. Hydrophobic regions exposed in this way would be expected to yield a higher contact angle than that observed on the bare surface.

Contact angle behavior among the surfaces of acrylic, polyester, polycarbonate and hydrophobic silicon was similar. Contact angles were observed to decrease upon contact with protein rather than increase as was observed with the more hydrophilic materials, indicating that the hydrophilicity of the film-covered surfaces is greater than that exhibited by their bare surfaces. Apparently, adsorption of protein can make hydrophilic surfaces more hydrophobic and hydrophobic surfaces more hydrophilic.

To some extent, the adsorption mechanism at hydrophobic surfaces can be characterized by so-called hydrophobic bonding. Hydrophobic regions of the protein interact with the hydrophobic surface, exposing hydrophilic regions at the surface of the film. This would be expected to make a film-covered surface more hydrophilic than its original surface.

A more quantitative criterion evolves from Fig. 2, a plot of the change in water contact angle upon film formation ($\Delta \theta_{water} = \theta_{film, ave} - \theta_{bare}$) vs. $W_{p, water}$ for each material. It is apparent that any material with $W_{p, water}$ greater than about 49 mJ/m$^2$, or less than about 37 mJ/m$^2$ will exhibit a $\Delta \theta_{water}$ greater than 5$^\circ$ upon film formation. A 5$^\circ$ difference in contact angle is taken as sufficient to distinguish a fouled material from a clean one by contact angle methods. In a similar fashion, it was found that 20% aqueous ethanol solutions will exhibit a $\Delta \theta_{20\% EtOH}$ greater than 5$^\circ$ when contacted with materials for which $W_{p, water}$ is greater than 52 mJ/m$^2$ or less than 39 mJ/m$^2$; 40% ethanol solutions were observed to be appropriate for materials with $W_{p, water}$ greater than 55 mJ/m$^2$, or less than 38 mJ/m$^2$. This indicates that diagnostic liquids have some measurable

Figure 2. Relationship between $\Delta \theta_{water}$ (= $\theta_{film, ave} - \theta_{bare}$) and $W_{p, water}$ for each material contacted with $\beta$-lactoglobulin. The two horizontal lines are drawn at $\Delta \theta_{water} = 5$ and -5$^\circ$.
Figure 3. Relationship between contact angle and adsorbed mass of milk for each solid surface: (a) glass, (b) #304 stainless steel, (c) acrylic, (d) polyester, and (e) polycarbonate. Open squares represent data recorded with water as diagnostic liquid, closed circles represent 20% EtOH, and open triangles represent 40% EtOH.

effect on observed $\Delta \theta$, and each liquid can be associated with a limitation regarding its use.

In summary, adsorption of $\beta$-lactoglobulin affects the surface character of the materials studied. Strongly hydrophilic surfaces become more hydrophobic, and strongly hydrophobic surfaces become more hydrophilic. Contact angle methods can detect the presence of films on such surfaces with the exception of those materials characterized by a value of $W^p_{water}$ between about 37 and 55 mJ/m$^2$.

Contact angles of aqueous ethanol solutions on milk films

Fig. 3a shows the relationship between contact angle and adsorbed mass for glass (only data recorded with water, 20% and 40% ethanol solutions are presented). Contact angles on film-covered surfaces are greater than those on the bare surface, as was the case with $\beta$-lactoglobulin films on glass. The results for #304 stainless steel are presented in Fig. 3b. Contact angles evaluated on fouled surfaces are greater than those on the bare surface, similar to the results obtained for glass. This indicates that a milk-fouled hydrophilic surface becomes less hydrophilic than its clean counterpart. Such a statement is supported by a milk-film model on #304 stainless steel proposed by Kane and Middlemiss (6), in which fat molecules, the major component left on the solid surface after cleaning (3,6), are present inside and mainly at the outer layer of the milk films. This would cause the milk film to behave like a hydrophobic surface.

As before, contact angles do not change with adsorbed mass in any clear manner. Contact angles of ethanol solutions on glass increase with adsorbed mass; contact angles of water on stainless steel apparently decrease with adsorbed mass. In any event, these changes in contact angle do not correlate well with adsorbed mass.

Figure 3c shows results obtained with acrylic. The contact angle of water increases with adsorbed mass at very low coverage, then decreases. As the film becomes thicker, some water molecules may penetrate into the film, making the apparent contact angle decrease. This would be consistent with the small molecular volume of water. In this case, the contact angle of water would not represent properties of the film-covered surface. Contact angles of ethanol solutions show a step increase upon milk adsorption, then an increasing trend with adsorbed mass, indicating that the surface becomes increasingly hydrophobic with increasing adsorbed mass. It seems that the presence of a film on the acrylic surface could be detected using ethanol solutions, but not water due to the penetration effect.

Figures 3d and 3e show results of the somewhat hydrophobic polymers, polyester and polycarbonate; these two polymers behaved in a similar fashion. Contact angles of water were observed to decrease with adsorbed mass, possibly due to penetration of water molecules into the porous milk film. Contact angles of the 40% ethanol solution were observed to increase at low surface coverage, then decrease with adsorbed mass. Intermediate concentrations of ethanol did not change with adsorbed mass in any clear manner.

A plot of $\Delta \theta_{water}$ vs. $W^p_{water}$ for milk film-covered surfaces is shown in Fig. 4. It indicates that if water is to be successfully used as the test liquid, $W^p_{water}$ for a given bare surface should be greater than 36 mJ/m$^2$ (if $\Delta \theta$ is to be 5$^\circ$ or more). Similar plots were constructed for 20 and 40% ethanol solutions (not shown). For the 20% ethanol solution, any material for which $W^p_{water}$ is greater than 30 mJ/m$^2$ should yield a $\Delta \theta$ greater than 5$^\circ$; for the 40% ethanol solution, $W^p_{water}$ should be greater than 32 mJ/m$^2$. In this case, limitations associated with use of these contact angle methods varied markedly with the diagnostic liquid chosen. In the case of acrylic (Fig. 3c), for which $W^p_{water}$ = 35.2 mJ/m$^2$, the 20 and 40% ethanol solutions successfully detected the presence of a film, whereas water did not. In the case of polyester and polycarbonate (Fig. 3d and 3e), contact angles were not observed to exhibit a well-defined
for each material contacted with milk. The two horizontal lines change upon film formation. In fact, these film-covered materials, even though their \(\Delta \theta\) is measured to be greater than 5°. In summary, for milk films formed on polyester and polycarbonate, use of contact angle methods were found to be inappropriate for evaluation of surface cleanliness. Contact angles do appear to assist detection of milk films on more hydrophilic materials, i.e., materials with \(W^p_{\text{water}} > 23\) mJ/m².

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