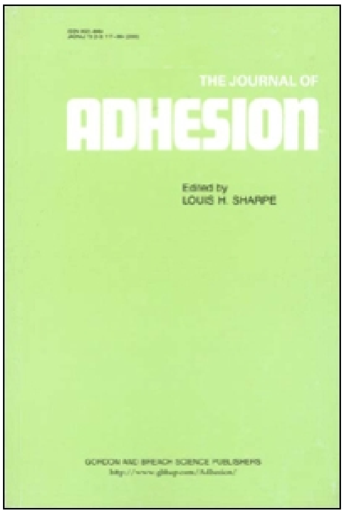

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Contact Angles and Monolayer Depletion

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ABSTRACT

Contact angles and contact angle hysteresis are very sensitive to surface heterogeneity. The degree of coverage of a surface by organic monolayers can be estimated by using the average of the cosines of advancing and receding angles in the equation of Cassie. This estimate can be refined by using a calibration curve computed from an idealized model of a heterogeneous surface.

Adhesion can be significantly influenced by the presence of monolayers and partial monolayers on adherends. These monolayers often control the rate of wetting by an adhesive and also the ultimate contact angle of the system. There is also some speculation that such monolayers might act as weak boundary layers.

Since contact angles are so sensitive to coverage by monolayers (1-2), the question arises as to what extent contact angles can be used to measure surface coverage. The work described in this paper was undertaken to answer that question. While the concepts developed here are applicable to any heterogeneous system, they were developed primarily to study the adsorption and depletion of organic monolayers on high energy surfaces.

THEORY

ALL THEORIES that relate surface coverage to contact angles depend ultimately on the assumption that the free energy of interaction of a liquid with a heterogeneous surface (e.g., partial monolayer of stearic acid on glass) is proportional to the fraction of the surface covered. While there is some question as to the universal validity of this assumption, especially when the heterogeneity is of molecular dimensions, a better one has not been suggested.

The work of adhesion between a liquid and a homogeneous solid (ignoring vapor adsorption) is

$$W_a = \gamma_{lg}(1 + \cos \Theta) \qquad (1)$$

where Θ is the contact angle (measured through the liquid) of the liquid on the solid and γ_{lg} is the surface tension of the liquid. On a homogeneous surface, there is only one measurable angle at equilibrium and W_a is well defined. A. B. D. Cassie[3] considered the heterogeneous system where a surface is composed of two sets of regions having contact angles Θ_1 and Θ_2. The fraction of the surface corresponding to Θ_1 regions is σ and that corresponding to Θ_2 is $(1\text{-}\sigma)$. The work of adhesion for this heterogeneous system being wetted by a liquid is

$$W_a = \gamma_{lg}[\sigma(1 + \cos\Theta_1) + (1\text{-}\sigma)(1 + \cos\Theta_2)] \tag{2}$$

Since equation 2 ignores adsorption from the vapor onto the surface, W_a is the work of adhesion for surfaces equilibrated with the vapor. Since we are concerned with contact angles on such surfaces, equation 2 is the proper one to use. Cassie essentially defined the "equilibrium" angle, $\hat{\Theta}$, as the angle which would be observed on a homogeneous surface with a work of adhesion equal to the average work of adhesion on the heterogeneous surface. Combining equations 1 and 2 yields Cassie's equation,

$$\cos\hat{\Theta} = \sigma\cos\Theta_1 + (1\text{-}\sigma)\cos\Theta_2 \tag{3}$$

Solving for σ yields

$$\sigma = \frac{\cos\hat{\Theta} - \cos\Theta_2}{\cos\Theta_1 - \cos\Theta_2} \tag{4}$$

Equation 4 would be extremely useful if it were possible to determine $\hat{\Theta}$ in a given system. Unfortunately, surface heterogeneity causes contact angle hysteresis which makes the determination of $\hat{\Theta}$ difficult if not impossible. The effect of surface heterogeneity on contact angle hysteresis is discussed in references 1 and 2. The problem of determining surface coverage from contact angle measurements is that of estimating $\hat{\Theta}$ from advancing and receding angles.

According to the concepts of references 1 and 2, hysteresis caused by surface heterogeneity depends on the sizes of the heterogeneous regions in the surface; the smaller the regions, the less the hysteresis. When the hysteresis is zero, the surface is homogeneous as far as contact angles are concerned. We give the name "homogeneous depletion" to the process where a monolayer is removed from the surface, either molecularly or in ultra-small patches, without the appearance of hysteresis. The patch size which does not generate hysteresis is not known but is probably under 50 A in diameter. When molecular or homogeneous depletion occurs, the coverage can be estimated from equation 4 using the measured contact angle for $\hat{\Theta}$. The calculated coverage must still be considered an estimate since it is with molecularly depleted monolayers that the assumption of proportionality between W_a and surface coverage is most in doubt.

We give the name "heterogeneous depletion" to the process in which the monolayer is removed in patches. As the depletion continues, the packing of the molecules in the patches (surface density) remains constant, but the sizes of the patches change.

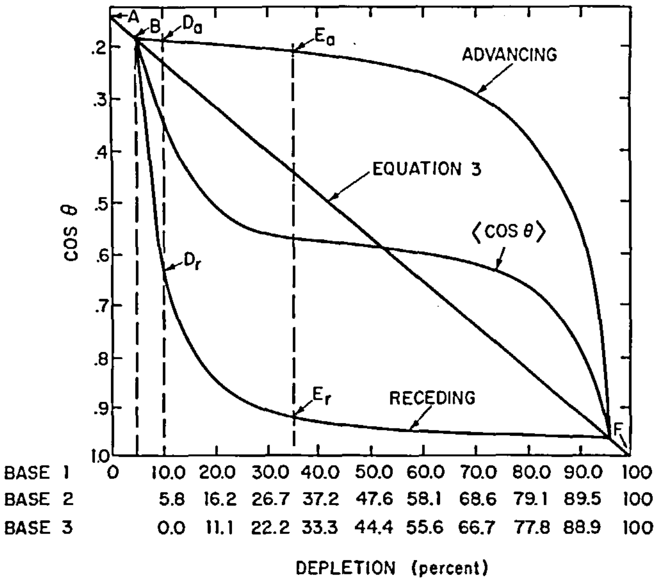

Figure 1: Effect of heterogeneous depletion of a monolayer on contact angle (idealized).

Depletion in real situations is probably never of one kind or the other but a mixture of both. This fact complicates the system and is a major limit on the ability to estimate coverage from contact angle measurements. Heterogeneous depletion is illustrated in Figure 1, where the cosine of the contact angle is plotted against depletion of the surface. Point A is the contact angle at maximum coverage, Θ_{max} (equal to 82° in this example). For monolayers Θ_{max} corresponds to a close-packed, uniform film. Point F is the contact angle on the completely depleted surface, Θ_{min} (equal to 0° in this example). The center line is a plot of equation 3 where $\Theta_1 = 82°$, $\Theta_2 = 0°$, and $100(1-\sigma)$ is the percent depletion. The advancing and receding angle curves were calculated using the method of reference 1 for an idealized heterogeneous surface. The magnitude of the hysteresis, $(\Theta_a - \Theta_r)$, where Θ_a is the advancing contact angle and Θ_r the receding angle, depends on the size of the heterogeneous regions. Point B is the depletion at which the patches are large enough to introduce hysteresis. We call the angle at Point B the Cassie angle, Θ_c (equal to 80° in the example). Other curves having similar shapes could be calculated by choosing different Cassie angles. Point D represents the maximum coverage that is obtained in a given set of experimental conditions. The angles at D_a and D_r are called the standard advancing, Θ_a°, and standard receding, Θ_r^{0}, angles respectively.

For example, a series of barium stearate monolayers deposited on a glass slide from a Langmuir trough might give average angles of 44.8° advancing and 43.1° receding with hexadecane. These would be the standard angles for this set of conditions. At a different pH of deposition, the average angles might be 43.1° advancing and 34.1° receding. These would be the standard angles for the new set of conditions. Point E represents angles after a depletion experiment. It is seen in figure 1 that it is possible to measure percent coverage with respect to three different reference states or bases. Base 1 gives the percent coverage with respect to point A, the ideal, complete monolayer. Base 2 gives the coverage with respect to point B, and base 3 is with respect to point D. Base 3 values are typically the kind used with other measuring techniques. For example, with radioactive monolayer depletion experiments the initial count corresponds to point D, the final count after depletion corresponds to point E, and the percent depletion would be calculated according to base 3.

As mentioned earlier, depletion is seldom either completely homogeneous or completely heterogeneous. In mixed depletion the intrinsic contact angle of the patches is decreased by molecular depletion. The advancing angle, which is closely related to this intrinsic angle, decreases more rapidly with depletion than is the case with heterogeneous depletion. Since homogeneous depletion can occur without changing the size of the patches, hysteresis is less. The hysteresis that is observed arises from the patchy structure originally found in the surface plus any changes that occur in the size of the patches during the depletion experiment. Figure 2 shows the contact angle behavior that would be expected for mixed depletion. Points A, B, D, and E have the same meaning as in Figure 1. It is seen that for the mixed depletion the hysteresis is less and the advancing angle is more sensitive to depletion than is the case with the heterogeneous depletion of Figure 1.

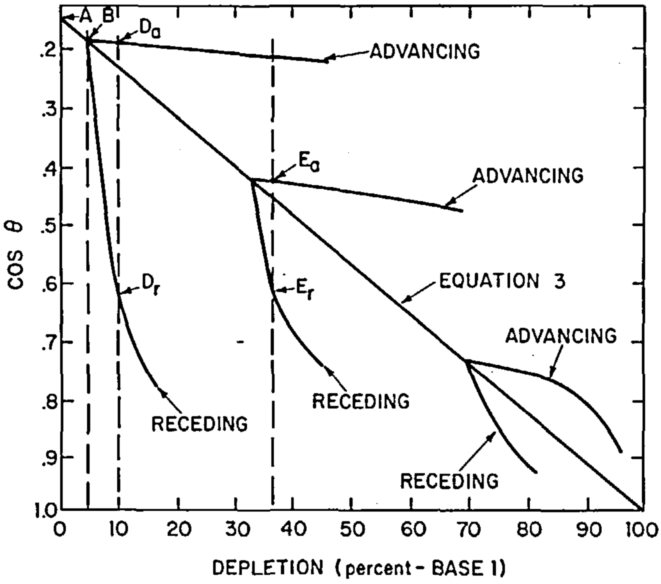

Figure 2: Effect of mixed depletion on contact angles for the system of Figure 1.

Our problem in all these cases is to estimate $\cos\hat{\Theta}$ from the advancing and receding angles. While it is apparent that neither the advancing nor receding angle is an adequate measure itself, the average of the cosines, $<\cos\Theta>$, is a possibility and is our first approximation to $\cos\hat{\Theta}$. Figure 1 shows $<\cos\Theta>$ for an idealized system. The coverage calculated using $<\cos\Theta>$ in place of $\cos\hat{\Theta}$ in equation 4 is called the coverage index, I. When calculated in terms of base 2, then

$$I_2 = 100\left(\frac{<\cos\Theta> - \cos\Theta_{min}}{\cos\Theta_c - \cos\Theta_{min}}\right) \tag{5}$$

where

$$<\cos\Theta> = \frac{\cos\Theta_a + \cos\Theta_r}{2}$$

We use subscripts to indicate bases 1, 2, and 3.

In Figure 3 coverage (base 2) is plotted against I_2 for the idealized system of Figure 1.

It is seen from Figure 3 that if I_2 were used as a measure of coverage, it would give an overestimate in regions of low coverage and an underestimate in regions of high coverage. It also re-emphasizes that contact angles are relatively insensitive to changes in coverage in the region from 25% to 75% coverage. The dotted, straight-line segments in Figure 3 are used for ease of calculation.

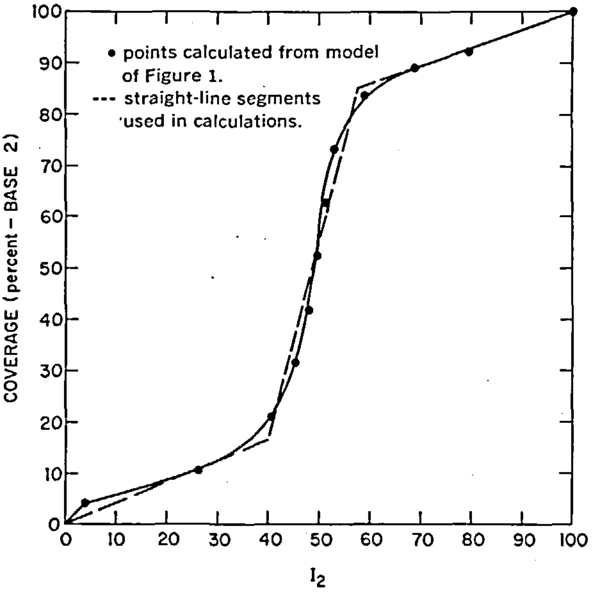

Figure 3: Coverage (base 2) vs. I_2 for the idealized system of Figure 1.

We define the coverage index relative to initial coverage (base 3) by the expression,

$$I_3 = 100\left(\frac{I_2}{I^0}\right) = 100\left(\frac{\langle\cos\Theta\rangle - \cos\Theta_{min}}{\langle\cos\Theta^{\circ}\rangle - \cos\Theta_{min}}\right) \tag{6}$$

where

$$\langle\cos\Theta^0\rangle = \frac{\cos\Theta_a^{\circ} + \cos\Theta_r^{\circ}}{2}$$

and

$$I^{\circ} = 100\left(\frac{\langle\cos\Theta^0\rangle - \cos\Theta_{min}}{\cos\Theta_c - \cos\Theta_{min}}\right) \tag{7}$$

I_3 has the distinct advantage of being derived from purely experimental quantities and is not dependent on any microscopic model. It is monotonic with coverage.

The coverage index relative to the ideal complete monolayer (base 1) is given by

$$I_1 = 100\left(\frac{\langle\cos\Theta\rangle - \cos\Theta_{min}}{\cos\Theta_{max} - \cos\Theta_{min}}\right) \tag{8}$$

It is possible to make corrections to I_2 with curves of the type shown in Figure 3. Since we do not have enough experimental data available to develop empirical curves, we will rely on the kind of theoretical curves developed in reference 1. Figure 3 can be considered to be a calibration curve relating coverage to I_2 or I°. While this curve was developed with $\Theta_{max} = 82°$, $\Theta_c = 80°$, and $\Theta_{min} = 0$, its shape is quite insensitive to the choice of these angles. This curve applies only to coverage indexes calculated for base 2. The three straight line segments in Figure 3 are given by

$$C_2 = A + B\,I_2 \tag{9}$$

where C_2 is the coverage in percent and

$A = 0, B = 0.425; 0 \leqslant I_2 < 40$
$A = -138.4, B = 3.885; 40 \leqslant I_2 \leqslant 57.5$
$A = 64.71, B = 0.3529; 57.5 \leqslant I_2 \leqslant 100.$

The coverage estimate based on the initial, or standard state (base 3) is given by

$$C_3 = \frac{100\,C_2}{C^{\circ}} \tag{10}$$

where C° is the coverage estimate based on the initial values of the contact angle. The coverage estimate based on the ideal complete monolayer (base 1) is given by

$$C_1 = C_2\left(\frac{I_1}{I_2}\right) \tag{11}$$

where I_1/I_2, the packing fraction, is given by

$$\frac{I_1}{I_2} = \frac{\cos\Theta_c - \cos\Theta_{min}}{\cos\Theta_{max} - \cos\Theta_{min}} \tag{12}$$

The name "packing fraction" was introduced by Shafrin and Zisman[4]. It is a measure of the coverage of the system at point B in Figure 1.

Coverage can also be estimated for the mixed mode of depletion in Figure 2, but the application of the correction curve is different. With this type of depletion we assume that the advancing angle for each set of measurements is the Cassie angle for that state of the system. With this approach

$$I_2'' = 100\left(\frac{<\cos\Theta> - \cos\Theta_{min}}{\cos\Theta_a - \cos\Theta_{min}}\right) \tag{13}$$

and

$$C_2'' = A + BI_2'' \tag{14}$$

I_2'' *is not very significant physically since it varies from 100% for* $\Theta_r = \Theta_a$ to 50% for $\Theta_r = \Theta_{min}$. In essence, it estimates the heterogeneous part of the mixed depletion. To estimate total depletion, C_2', it is necessary to multiply C_2'' by the homogeneous depletion factor with respect to base 2,

$$C_2' = C_2''\left(\frac{\cos\Theta_a - \cos\Theta_{min}}{\cos\Theta_c - \cos\Theta_{min}}\right) \tag{15}$$

The coverage estimate based on the initial coverage is given by

$$C_3' = 100\,\frac{C_2'}{C^{o\prime}} \tag{16}$$

where $C^{o\prime}$ is calculated from equations 13, 14, and 15 using $\Theta_a{}^o$ and $\Theta_r{}^o$ for Θ_a and Θ_r respectively. It is often the case that the Cassie angle is equal to $\Theta_a{}^o$. For this case

$$C^{o\prime} = C^o \tag{17}$$

The coverage estimate based on the ideal complete monolayer in the mixed depletion model is given by

$$C_1' = C_2'\left(\frac{I_1}{I_2}\right) \tag{18}$$

It can be seen from the above discussion that contact angles alone are insufficient to accurately determine the coverage of a surface. In addition to heterogeneity, surface roughness and surface deformability influence contact angles. Interaction of wetting solvents with surfaces through adsorption or desorption can also have a marked influence on the angles. Even with these limitations, however, we find that contact angles give much useful information about surface coverage. Of course, the more information that is initially available about the surface, the more meaningful will be the interpretation of angles. In the absence of such information, probability considerations would suggest that the mixed depletion method of estimation be used. This follows from the fact that the advancing contact angle is relatively insensitive to coverage over about 80 percent of its range. Therefore, without other knowledge, the probability is about 0.8 that the advancing angle is equal to or very close to the Cassie angle for that state of the system. In general, the most significant coverage estimate is that which is given as a percent of an initial or standard state (C_3 or C_3'). This eliminates the uncertainty associated with estimating the contact angle of close-packed, ideal monolayers and is the value usually used when comparing the wettability method with other techniques.

The usefulness of this technique for estimating coverage can only be determined by experimental measurements on heterogeneous systems. The balance of this paper describes two applications we have made.

EXPERIMENTAL

An experimental system used to evaluate the equations for heterogeneous depletion consists of very small patches of titania on glass with trimethyloctadecylammonium chloride adsorbed only on the uncovered glass surface. The experimental details and the data used in our calculations are given in reference 2 and will not be repeated here.

A system which has all the characteristics of mixed depletion is the hydrolysis in air (50% relative humidity) of a film of polydibutyl titanante. The hydrolysis products are butyl alcohol and titania (anatase). The polydibutyl titanate was Du Pont Tyzor® PB organic titanate. Coatings were formed on soda-lime glass microscope slides (Thomas Red Label brand; 2.5 x 7.6 cm.). The slides were coated from both 2.1 v/v% and 10.0 v/v% solutions of the organic titanate in CCl_4 using a Fisher-Payne Dip-Coater. Triplicates were run for the coating from the 2.1 v/v% solution and duplicates for the coating from the 10.0 v/v% solution coating. The hydrolysis rate was increased slightly by immersion in water. Separate experiments in which the slides were rinsed with water showed that contact with water during the measuring process did not introduce significant errors.

Water contact angles on both these systems were measured at 25±1° and 50±5% relative humidity by the sessile-drop technique. Average drop size was 0.05 ml. Advancing and receding angles were obtained as previously described[2].

RESULTS AND DISCUSSION

Heterogeneous Depletion

The system trimethyloctadecylammonium chloride on titania-coated glass provides an experimental example of heterogeneous depletion. The evidence presented in reference 2 strongly suggests that trimethyloctadecylammonium chloride adsorbs on glass but not on titania. Under the conditions of the experiments described in reference 2, trimethyloctadecylammonium chloride adsorbs on glass to give an advancing angle of 64° and a receding angle of 39° with water. This is our initial or standard state against which other measurements are compared. As the titania coverage increases, the fraction of the surface coated with the hydrophobic trimethyloctadecylammonium chloride decreases, resulting in lower contact angles.

Figure 4 gives the coverage of the surface by trimethyloctadecylammonium chloride plotted against three different measures of depletion; I_3, C_3, C_3'. The coverage by the monolayer was estimated from the titania coverage given in reference 2. The best agreement is with the heterogeneous depletion model, C_3, as would be expected from other knowledge of the system[2]. The deviation from the straight, ideal line at low monolayer (high titania) coverage is caused by uncertainties in the coverage estimates of titania, which are greatest at high coverages, and also by the uncertainties in the model. If any trimethyloctadecylammonium chloride adsorbed on the titania as well as on the glass, the expected effect on wettability would cause a deviation in the direction seen in Figure 4.

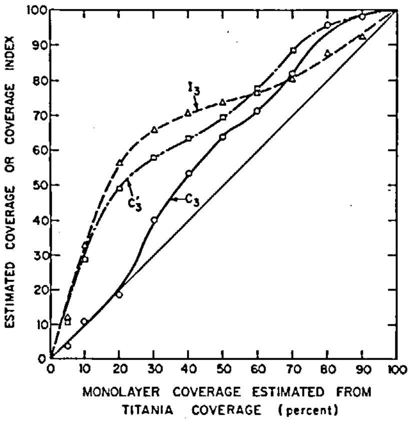

Figure 4: Comparison of coverage by trimethyloctadecylammonium chloride monolayer estimated from contact angles with that estimated from titania coverage.

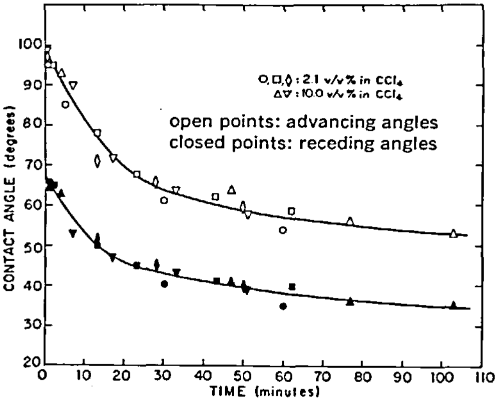

Figure 5: Water contact angles on polydibutyl titanate as a function of time.

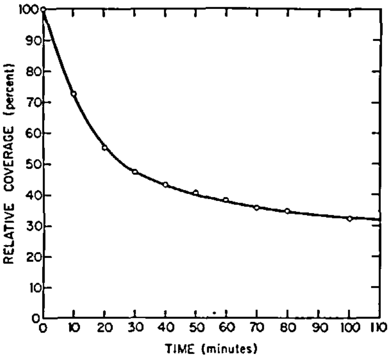

Figure 6: Relative coverage (C_3') vs. time for the hydrolysis of polydibutyl titanate using the mixed depletion model.

Mixed Depletion

The hydrolysis of polydibutyl titanate to titania and butyl alcohol is an example of a system which is consistent with the mixed depletion model. Figure 5 gives contact angles of water on polydibutyl titanate coatings on glass as a function of the time the coating has remained at 50% relative humidity and 25°C. The hysteresis decreases with time, and the curves do not suggest the kind of depletion shown in Figure 1.

In Figure 6 C_3', the relative coverage by the organic titanate (referred to the contact angles at time zero), is plotted against time.

Figure 7 shows how the observed contact angles at 0, 10, 20, and 70 minutes can be fitted onto a homogeneous depletion curve to give a behavior similar to that of Figure 2 for the mixed mode of depletion. The homogeneous depletion curve is given by equation 3, where $\Theta_1 = 105°$ and $\Theta_2 - 0°$. An angle of 105° is an estimate of the contact angle of water on a surface completely covered (base 1) by polydibutyl titanate.

It should be emphasized that this system does not represent a test of the model since there is no independent measure of coverage. It does, however, show that the mixed depletion model gives a reasonable description. We are currently testing the model by determining the wettability of radioactive monolayers. These data will be published shortly.

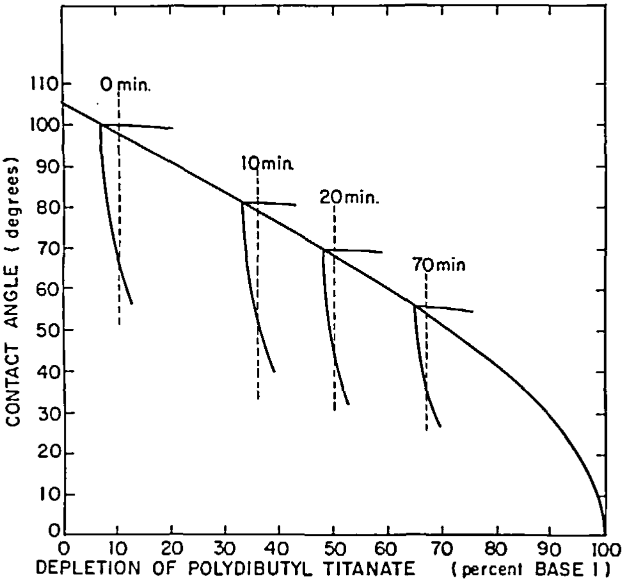

Figure 7: Mixed depletion model for the hydrolysis of polydibutyl titanate.

NOMENCLATURE

θ	Contact angle
θ_{max}	Maximum possible contact angle of the system
θ_{min}	Minimum possible contact angle of the system
$\hat{\theta}$	The most stable or equilibrium angle (given by equation 3)
θ_a^o	The standard advancing angle
θ_r^o	The standard receding angle
θ_c	The Cassie angle (i.e., the smallest angle of the system for which there is no hysteresis)
I_2	The coverage index with respect to the Cassie angle

$$I_2 = 100\left\{\frac{<\cos\theta> - \cos\theta_{min}}{\cos\theta_c - \cos\theta_{min}}\right\}$$

I°	The coverage index of the standard experimental state

$$I^\circ = 100\left\{\frac{<\cos\theta^\circ> - \cos\theta_{min}}{\cos\theta_c - \cos\theta_{min}}\right\}$$

I_3	The coverage index relative to I°

$$I_3 = 100\left\{\frac{I_2}{I^\circ}\right\}$$

I_1 The coverage index relative to the ideal complete monolayer.

$$I_1 = 100\left\{\frac{<\cos\Theta> - \cos\Theta_{min}}{\cos\Theta_{max} - \cos\Theta_{min}}\right\}$$

C_2 The coverage estimate (heterogeneous model) relative to the Cassie angle obtained using the calibration curve of Figure 3,

$$C_2 = A + BI_2$$

C° The coverage estimate (heterogeneous model) for the standard experimental state relative to the Cassie angle

$$C^\circ = A + BI^\circ$$

C_3 The coverage estimate (heterogeneous model) relative to the standard experimental state.

$$C_3 = 100\,\frac{C_2}{C^\circ}$$

C_1 The coverage estimate (heterogeneous model) relative to the ideal complete monolayer.

$$C_1 = C_2\left(\frac{I_1}{I_2}\right)$$

I_1/I_2 The packing fraction

C_2' The coverage estimate (mixed model) relative to the Cassie angle.

$$C_2' = \left[A + 100B\left\{\frac{<\cos\Theta> - \cos\Theta_{min}}{\cos\Theta_a - \cos\Theta_{min}}\right\}\right]\left\{\frac{\cos\Theta_a - \cos\Theta_{min}}{\cos\Theta_c - \cos\Theta_{min}}\right\}$$

$C^{\circ\prime}$ Coverage estimate (mixed depletion model) of standard experimental state.

C_3' The coverage estimate (mixed depletion model) based on experimental standard state.

$$C_3' = 100\,\frac{C_2'}{C^{\circ\prime}}$$

C_1' The coverage estimate (mixed depletion model) based on the ideal complete monolayer.

$$C_1' = C_2'\left(\frac{I_1}{I_2}\right)$$

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