Contact angle relaxation for ethoxylated alcohol solutions on hydrophobic surfaces

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Abstract—The measurements of contact angles for ethoxylated alcohol solutions on hydrophobic toner and polyethylene surfaces were carried out using the sessile-drop technique. The drops of aqueous ethoxylated alcohol (C_{12}H_{25}(C_{2}H_{4}O)_{n}OH; n=4 to 7) solutions, with a concentration ranging from 1 μM to 1 mM, were used and the contact angle relaxation was recorded over a period of 30 minutes. It was found that the contact angle relaxed significantly in the first few minutes and the relaxation was substantially reduced thereafter. The kinetics of contact angle relaxation could be described by a power law equation of the type: \( \theta(t) - \theta(0) = \text{constant} \times t^{m} \), where \( \theta \) is the contact angle, \( t \) is the time and \( m \) is the relaxation rate constant. It was also found that the contact angle relaxation depended on the surfactant concentration (C). An empirical correlation between \( m \) and \( C \) was determined from the contact angle relaxation data as follows: \( m = aC^{b} \), where \( a=10-20 \) and \( b=0.44-0.57 \).

Keywords: Contact angle relaxation; deinking flotation; ethoxylated alcohol; hydrophobic surfaces; paper recycling.

1. INTRODUCTION

In de-inking flotation of wastepaper pulp, hydrophobic ink particles are collected by air bubbles and transported to a froth layer. Surface active chemicals control the surface tension of water and froth stability. Ethoxylated alcohols are among the popular surfactants selected for this application in US paper recycling plants [1-3]. The frothing potential of ethoxylated alcohol surfactants is well known, however, the effect of these chemicals on the properties of hydrophobic ink particles has not been examined. In this regard, systematic measurements of contact angles for ethoxylated alcohol solutions on hydrophobic toner and polyethylene surfaces were undertaken in this study using the sessile-drop technique.

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The wettability of hydrophobic surfaces by surfactant solutions has been extensively studied in recent years [4-11], including studies on the wetting of toners [12-14]. The results from "static" contact angle measurements indicate that the contact angle versus surfactant concentration (θ vs. log C) relationship is similar in shape to the surface tension versus surfactant concentration isotherm for aqueous surfactant solutions [8-10]. Specifically, the contact angle changes by only a few degrees with increasing surfactant concentration for diluted surfactant solutions. Next, at moderate surfactant concentration, the slope of the θ vs. log C curve becomes larger. Finally, at a certain surfactant concentration, the contact angle remains unaffected by increasing surfactant concentration. The experimental results for several systems indicate that the transition from a sharp slope of the θ vs. log C curve to a plateau occurs at the critical micelle concentration (cmc) for the surfactant [8, 9]. In contrast to this behavior, transition points above the cmc have also been reported [10].

Studies on the wetting of hydrophobic surfaces by surfactant solutions indicate that three-phase systems become unstable over some time, and this instability is associated with adsorption and rearrangement of surfactants at solid-liquid and liquid-fluid interfaces [5-7]. It was thus important in this project to undertake the contact angle measurements over an extended period of time. As a result, further support for contact angle relaxation of surfactant solutions at solid surfaces is provided in this contribution.

It should be mentioned that the time-scale for contact angle relaxation in this study is different from that observed by Haidara and coworkers [6, 7]. Moreover, the experimental system and experimental procedures used in this study differ significantly from those used by Haidara and coworkers, thus no direct comparison between the results from these two different studies is recommended. For example, Haidara and coworkers [6, 7] reported contact angle relaxation results for an organic liquid drop that was placed on a hydrophobic surface immersed in water. The surfactant solution was injected into water at a certain distance from the organic liquid drop. In contrast, in our study, the surfactant solution drop was placed directly on the hydrophobic surface. Thus, the equilibration of the surface with the surfactant solution is much faster in our study than that observed in other investigations [6, 7].

In this paper, examples of contact angle relaxation are reported for a broad range of ethoxylated alcohol concentrations, from 1 µM to 1 mM. It was found that the kinetics of contact angle relaxation for dilute solutions differed substantially from the kinetics for saturated solutions carrying surfactant micelles.

2. MATERIALS AND METHODS

Low-density polyethylene powder, with a molecular weight of 6500 and a softening point of 110°C, was purchased from Scientific Polymer Products, Inc. Xerox Dry Ink Plus 5052/1050 (softening point about 80-90°C) composed of 85-90%
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A styrene/acrylate polymer, 10-15% carbon black, <1% amorphous silica and <1% zinc stearate was used as a model toner in this study. High purity polyethylene glycol monoalkyl ethers, C₁₂E₄ (n=4 to 7), were purchased from Nikko Chemicals (Tokyo, Japan). Deionized and filtered water was used to prepare the solutions.

Smooth polyethylene and toner samples were prepared by heating the polymeric material on glass slides and pressing with a glass slide (polyethylene) or mica sheet (toner). Polymer substrates were separated from the glass surface in water. As the water spreads well over the surfaces of both mica and glass, removal of the polymer samples from mica and glass is relatively easy. The polymer samples were washed with water, dried and stored in air. A polyethylene cover was placed over the polymer samples to avoid the deposition of dust particles from the laboratory environment. The samples were stored at least one day before contact angle experiments.

The surface roughness and wettability for prepared polyethylene and toner samples are shown in Table 1. RMS is the root-mean-square roughness, \( R_a \) is the average roughness, \( R_{\text{max}} \) is the maximum height (the difference in heights between the highest and lowest points on the surface relative to the center plane), \( \theta_a \) is the advancing water contact angle, \( \theta_R \) is the receding water contact angle, and \( \Delta \theta = \theta_a - \theta_R \) is the contact angle hysteresis. RMS and \( R_a \) are defined as follows:

\[
RMS = \sqrt{\frac{\sum (Z_i - Z_{\text{av}})^2}{N}}
\]

\[
R_a = \frac{1}{L_x L_y} \int_0^{L_y} \int_0^{L_x} f(x, y) dxdy
\]

where \( Z_{\text{av}} \) is the average of the \( Z \) values (elevations) within the given area, \( Z_i \) is a specific \( Z \) value, \( N \) is the number of points within the given area, \( f(x, y) \) is the surface relative to the center plane, and \( L_x \) and \( L_y \) are the dimensions of the surface along \( x \) and \( y \) coordinates. The roughness characterization was carried out using a MultiMode Atomic Force Microscope from Digital Instruments, Inc.

A polymer sample was placed in a transparent polycarbonate cell on a flat ceramic support. Water was poured in the bottom of the cell and the top was sealed with a thin paraffin foil to prevent evaporation of the drop under examination and

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS [nm]</th>
<th>( R_a ) [nm]</th>
<th>( R_{\text{max}} ) [nm]</th>
<th>( \theta_a ) [deg]</th>
<th>( \theta_R ) [deg]</th>
<th>( \Delta \theta / \Delta (\cos \theta) ) [deg]/-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toner</td>
<td>8.5±3.3</td>
<td>6.2±1.8</td>
<td>194±160</td>
<td>87±2</td>
<td>70±3</td>
<td>17±4/-0.290</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>69±11</td>
<td>55±10</td>
<td>420±55</td>
<td>92±2</td>
<td>75±2</td>
<td>18±3/-0.294</td>
</tr>
</tbody>
</table>
to maintain water-saturated conditions in the cell. The 0.5 mm needle of the microsyringe was situated just above the polymer sample, through a small hole in the cover. A 20-40 µL drop of the solution was placed on the surface of the polymeric disk. An image of the drop was taken with a Krüss Contact Angle Measuring System G 10. Using Drop Shape Analysis software, a curve was fitted to the drop perimeter using the Young-Laplace equation. The contact angle was then determined from the slope of the contour line at the three-phase boundary point.

3. RESULTS AND DISCUSSION

3.1. Contact angle relaxation

Contact angle relaxation occurred for drops of all surfactant solutions used in this study. The value of the contact angle gradually decreased over a period of several minutes as shown in Figures 1 and 2 for polyethylene and toner, respectively. On both surfaces, polyethylene and toner, the contact angle relaxation increased with increasing surfactant concentration. Two different regimes of contact angle relaxation were observed (Figure 3): the fast and slow kinetic regions. The driving force for the spreading of a liquid drop over a solid surface comes from the difference between dynamic (θ) and equilibrium (θo) contact angles [15-17]:

\[ \text{spreading} \sim \gamma_{LV}(\cos \theta_o - \cos \theta) \]

where \( \gamma_{LV} \) is the surface tension of the liquid. Because the difference between dynamic and equilibrium contact angles diminishes with time, the rate of contact angle relaxation decreased over the time of the experiment (Figures 1 to 3).

![Figure 1](image-url)  
Figure 1. Selected contact angle relaxation results for C_{12}E_{5} solutions on polyethylene. Concentrations of C_{12}E_{5} solutions were 10^{-6} M, 10^{-5} M, 5x10^{-5} M, 10^{-4} M, and 10^{-3} M, for the results from the top to bottom of the figure.
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Figure 2. Selected contact angle relaxation results for $C_{12}E_4$ solutions on toner. Concentrations of $C_{12}E_4$ solutions were $10^{-6}$ M, $5 \times 10^{-5}$ M, $10^{-4}$ M, and $10^{-2}$ M, for the results from the top to bottom of the figure.

Figure 3. Kinetics of contact angle relaxation for $1 \times 10^{-4}$ M $C_{12}E_6$ solution on polyethylene.

The results shown in Figures 1 to 3 indicate that the three-phase contact angle was in a dynamic state over the entire period of the experiment (30 min), trying to reach a shape to minimize the total energy of the three-phase system. The slow relaxation of the triple contact line was observed even for pure water and is consistent with previous observations [18]. Any surface defects, arising from heterogeneity or roughness, will cause such contact angle relaxation phenomenon [18].
Both substrates used in this study were rough at the nano-scale level (Table 1). The toner surface was smoother than polyethylene surface, but probably more heterogeneous due to the multi-component composition of the toner [19, 20].

The presence of surfactants adsorbing at interfaces makes the analysis of the data even more complicated. The spreading time was found to be strongly dependent on the surfactant concentration (Figures 1-3). This clearly indicates that these surfactants affected the kinetics of contact angle relaxation. As shown from a simplified picture (Figure 4), surfactant adsorption at a hydrophobic surface (and air) takes place mainly through the interaction of surfactant hydrocarbon chains, with the polar segment of surfactant (composed of hydroxylated ethoxy groups in this case) accommodated by the aqueous phase. During the spreading of surfactant solution over the substrate, the hydrophobic surface is constantly covered by the solution and the adsorption of surfactant molecules must progressively take place on the freshly covered area of the solid surface [21-23]. Thus, the kinetics of surfactant adsorption on the hydrophobic surface could have a profound effect on the kinetics of drop spreading. The mechanism of surfactant adsorption at these hydrophobic surfaces is not clear at this moment but deposition of ethoxylated alcohol molecules must occur as the three-phase line of contact region is extended. As schematically shown in the left upper corner of Figure 4, the deposition of the surfactants at the solid surface might progress through the “rolling” solution-air interface.

Figure 4. Illustration of major mechanisms occurring during the spreading of a droplet of surfactant solution over a solid substrate. Arrows indicate the reduction of surfactant concentration inside the drop and its adsorption at solution-air and solid-solution interfaces. Also note that a precursor film, which might be present in front of the spreading drop [21, 22], is not shown in this simplified drawing.
Also, the kinetics of adsorption at the liquid-air interface might have an effect on the contact angle relaxation at the beginning of the spreading process (Figure 4). It is not, however, the major factor that should be considered in the interpretation of the experimental data. According to independent surface tension measurements performed in the same research program using a pendant drop technique, only several seconds were required to saturate the solution-air surface with an adsorbed ethoxylated alcohol. Also recently, a study of the kinetics of ethoxylated alcohols adsorption at the water-air interface has been published by Zhmod et al. [24], which supports this finding.

The spreading of the drop enlarges both solution-air and solid-solution interfacial areas leading to a depletion of surfactant concentration inside the drop. This effect results from the adsorption of surfactants on freshly created interfaces. As a consequence, both the kinetics of drop spreading and contact angle values are certainly affected by competition between the retention of surfactants and their adsorption at extended interfaces. Because the decrease in the surfactant concentration in the bulk of the drop due to adsorption can be as large as $10^{-6}$ to $10^{-4}$ M, depending on the initial surfactant concentration, the depletion/adsorption process is expected to have a significant effect on the results shown in Figures 1-3.

It is also believed that the contact angle relaxation phenomenon is, at least partially, the result of the molecular changes occurring in the region of the three-phase line of contact. As discussed in the previous paragraph, the adsorption of ethoxylated alcohol molecules probably continues to a certain extent over the entire experiment. Also, rearrangements and conformational changes of molecules at the solid-liquid interface probably caused changes in the contact angle.

As shown in Figures 1 and 2, the concentration of ethoxylated alcohol has a strong effect on the $\theta$ vs. $t$ relationship. Assuming that the drop is in contact with the pure hydrophobic surface at the first moment, it is in contact with a layer of adsorbed ethoxylated alcohol at the advanced stage of the spreading process. As ethoxy groups are more likely to be oriented into the aqueous phase, the formation of an adsorbed layer of increased density leads to an increased hydrophilicity of the surface. However, whether contact angles relaxed differently for different surfactant concentrations could not be directly deduced from Figures 1 and 2. The appropriate theoretical model that would describe the experimental data from this study is not yet available to the authors. Thus, in order to compare the experimental contact angle results for systems of varying surfactant concentration, an empirical approach was used. In this study, several fitting functions were tested, including: i) $\theta=f(\log(t))$, ii) $\theta=f(t^m)$, iii) $\log\theta=f(t)$, iv) $\log\theta=f(\log(t))$, v) $\cos\theta=f(t)$, and vi) $\log(\cos\theta)=f(\log(t))$. It was found that the results could be described by the log-log function: $\log\theta=f(\log(t))$ (see Figure 5 for example); although the $\log(\cos\theta)$ versus $\log(t)$ function also provided a reasonable fit to the experimental data.

Assuming that the contact angle relaxation results follow a power law relationship: $\theta \sim t^m$, the $m$ values were calculated (called the relaxation rate constant in the
next part of this report) for most of the experimental data and plotted as a function of initial surfactant concentration (C) (Figure 6). Again, the experimental results were fitted to an empirical power function and it was found that the relationship between \( m \) and \( C \) could be described by the following equation: \( m = aC^b \) where \( a = 10 \) and \( b = 0.44 \) for \( C_{12}E_4 \) solutions on toner, and \( a = 20 \) and \( b = 0.57 \) for \( C_{12}E_5 \) solutions on polyethylene. A fitting line for all experimental results shown in Figure 6 could be drawn using the approximate function as \( m \approx 12C^{0.5} \).

The results in Figure 6 clearly indicate that there is only a little effect of surfactant concentration on the contact angle relaxation rate constants for the spreading of drops with a surfactant concentration less than the cmc. The rate of contact angle relaxation increased substantially for solutions carrying dispersed micelles of ethoxylated alcohol. This suggests that the mechanism of drop spreading for solutions with monomers and micelles differs not only due to the concentration depletion in the bulk and adsorption of molecules at the interfaces but also due to possible differences in the mechanisms of ethoxylated alcohol adsorption and the formation of different surface micelle structures as has been reported in the literature [25-28]. The structures formed at the polyethylene and toner surfaces were not investigated in this study. As shown in Figure 7, we speculate that the adsorbed ethoxylated alcohol molecules rest in a flat orientation at low surfactant concentrations. Organized molecular structures of ethoxylated alcohol are probably formed at surfactant concentrations larger than about \( 10^{-4} \) M. Also, a transition from the monomolecular layer to a worm-type structure could take place at concentrations close to or larger than the cmc [25-28].
Figure 6. The effect of surfactant concentration on the contact angle relaxation rate constant. Circles, squares, and triangles represent the experimental data for \( C_{12}E_5 \) solutions on polyethylene, \( C_{12}E_4 \) solutions on toner, and \( C_{12}E_5 \) solutions on toner, respectively.

Figure 7. A possible description for adsorption of nonionic surfactants on hydrophobic surfaces.

3.2. Static contact angle versus surfactant concentration

The contact angles that stabilized after 30 minutes of relaxation were used for the correlation between the "static" contact angle and (initial) ethoxylated alcohol concentration. These contact angles should not be mistaken with "equilibrium" (or Young's) contact angles for perfectly equilibrated and saturated systems. As shown in the previous section, the contact angle relaxation process was not com-
pleted in 30 minutes of the experiment. Nevertheless, the contact angles measured after 30 min are assumed to be very close to equilibrium contact angles, and these values were used for comparison.

Examples of the relationship between contact angle and ethoxylated alcohol concentration are shown in Figures 8 and 9 for polyethylene and toner, respectively when surfactant ratio concentration effect concentration is present.

Across the used point, agreement between alcohol surfactant appears (Figure 8). It serves the contribution is mechanical, possibly saponified surfactant.

Figure 8. The effect of ethoxylated alcohol concentration on static contact angles measured after 30 min for $C_{12}E_5$ (diamonds) and $C_{12}E_7$ (squares) solutions on polyethylene.

Figure 9. The effect of ethoxylated alcohol concentration on contact angles measured for $C_{12}E_4$ solutions on toner after 1 and 30 minutes.
tively. These relationships are similar to the graphs presented by others [8-10] where it was shown that the $\theta$ vs. $\log C$ relationship was similar in shape to the surface tension isotherms reported for aqueous surfactant solutions. The results shown in Figures 8 and 9 support this observation. Specifically, the dilute concentrations of ethoxylated alcohols had little effect on contact angle. The slope of the contact angle versus surfactant concentration becomes sharp at moderate concentrations of ethoxylated alcohol, about $1\times10^{-5}$ to $1\times10^{-4}$ M solutions. A negligible effect of ethoxylated alcohol concentration on contact angle was observed for concentration exceeding $1\times10^{-4}$ M.

However, the results reported in this contribution suggest possible differences between the systems reported in the literature [8, 9] and the ethoxylated alcohols used in this study. The most striking difference is the location of the transition point between the sharp slope and the plateau region on the $\theta$ vs. $\log C$ curve. In agreement with the systems examined by Wustneck and Wasow [10], the transition point was located above the cmc of the surfactant used. For ethoxylated alcohol solutions placed on both polyethylene and toner substrates the transition point appeared at concentrations a few times larger than the cmc of ethoxylated alcohol (Figures 8 and 9). This cannot be the result of dynamic effects as this was observed practically at all stages of contact angle relaxation (Figure 9). Also, since the number of monomers does not change above the cmc, this effect cannot be attributed to mass transfer, especially in view of the fact that contact angle relaxation increases for concentrated solutions as discussed in the previous section. The mechanism of depletion of the surfactant concentration in the drop bulk is one possibility that might be considered. Another mechanism involved could be formation of different molecular configurations at the hydrophobic surface at different surfactant concentrations [25-28].

Further, a deflection point in the contact angle versus initial surfactant concentration and located at approximately the cmc was sometimes observed (Figure 9). This also suggests a transition in surface structure of the aggregated surfactants. Such an interpretation is supported by recent studies in which these structures have been imaged in-situ by AFM techniques [25-28].

4. CONCLUSIONS

It was found in this study that drops of aqueous ethoxylated alcohol ($C_{12}H_{23}$ ($C_2H_4O)n$OH; n=4 to 7) solutions at hydrophobic surfaces of polyethylene and toner exhibited a relaxation of the contact angle. The contact angle relaxation was found to be described by a power function; $\theta(t)-\theta_e(t=0)=\text{constant} \times t^m$. The contact angle relaxation constant ($m$) was found to be strongly influenced by the concentration of surfactant according to the following equation, $m=\alpha C^b$ where $\alpha=10-20$ and $b=0.44-0.57$, for ethoxylated alcohol concentration less than 1 mM. It was also found that the kinetics of spreading of the solutions with ethoxylated alcohol
concentration greater than the critical micelle concentration was faster than the spreading observed at lower concentrations, prior to micelle formation.

Acknowledgments

The financial support from the U.S. National Science Foundation through a grant (CTS-9618582) awarded to the University of Utah is acknowledged with thanks. Also, the authors would like to thank the referees for several valuable comments and Dr. Mittal for additional corrections of the manuscript. RZ appreciates training in operation of the AFM instrument provided by Elvin Beach.

REFERENCES