WETTING OF MIXED FILMS OF FATTY ACIDS BY HEXADECANE

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INTRODUCTION

Previous investigations (1) have shown that in certain, well-defined systems, the wettability of a solid covered by an adsorbed film is not appreciably changed upon removing a substantial amount of the adsorbed film. One of the requirements for this behavior is that the wetting molecules must be able to enter the holes created in the film by depletion and become an integral part of the film. This requirement was demonstrated by showing that the wettability of octadecylamine films increased when hexadecane was replaced as the wetting liquid by molecules of similar surface tension but differing molecular structure.

The ability of the adsorbed film, even though severely depleted, to maintain a framework in which the wetting molecules may orient is also a requirement for the above mentioned wetting behavior. This requirement was partially demonstrated by showing that adsorbed films of dodecylamine were not capable of orienting the wetting molecules to such an extent as the longer octadecylamine molecules.

The present study was undertaken to investigate the wetting of adsorbed acid films as a function of the extent of adsorption when the ordering of the films was disturbed. In particular, the ability of the adsorbed acid films to maintain a substantial framework on depletion was tested by the inclusion of differing length and nature acid molecules. A combined optical and radiochemical technique was used to assess the acid composition of the films at each degree of film coverage.

EXPERIMENTAL

Materials. Triple-plated, chrome-finished ferrotype plates were cut for slides and cleaned as in previous studies (1) for film formation.

Hexadecane used for contact angle measurements was purified by the procedure of Zisman *et al.* (2).

Laboratory supply distilled water was made 10^{-4} molar in $BaCl_2$ for film formation and had a resultant pH of 6.6.

Stearic acid-1-C 14 and myristic acid-1-C 14 were obtained from the Nuclear Chicago Corporation and were reported as 99 and 98%

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radiochemical purity in benzene solutions. The respective specific activities were 21.7 and 2.55 mc./mM. and were diluted further with benzene to suitable concentrations for film formation.

Stearic acid having a m.p. of 68.5-69.0° C and capric acid having a m.p. of 29-30° C were used in mixed films with the tagged acids.

Film formation. The Blodgett (3) technique was used for film formation. Benzene solutions of the acids were mixed in the desired ratio and placed on the aqueous surface at 18 ± 1° C. This temperature appeared to give maximum contact angles for complete myristic acid films. The piston oils, castor oil and oleic acid, did not function properly at lower temperatures and the myristic acid was too soluble at higher temperatures. At the pH and temperature of film formation, the solubility of the myristic acid in the substrate is quite dependent on the ions in the substrate (4, 5).

Optical measurements. The instrument used for measuring the total film density was essentially the one used in a similar study (1). An angle of incidence of 67° was used.

Optical readings were taken shortly after cleaning the slides and immediately before film formation. After contact angle and radiochemical measurements, the slides were depleted by a rapid benzene dip and another optical reading taken.

Contact angle measurements. A 10 cc. syringe was used in conjunction with a rack and pinion device to advance and recede hexadecane drops across the films. A filmstrip projector was used to project the drop images on a piece of white paper. The base and tangent lines were drawn on the paper and the angles were measured later.

Care was taken to avoid the areas used in the counting process. Reproducibility at several areas was usually ± 1° for complete films and ± 2° for depleted films.

Radiochemical measurements. A windowless, nonshielded gas flow chamber was used with a conventional scaling unit. The slide was placed in a reproducible position resting on a solid polyethylene disk and masked by a polyethylene disk with a 1.4 cm.² hole and Q gas was passed through the chamber. Background counts were taken for each measurement and the system was cleaned frequently by flushing with Q gas passed through ethanol.

RESULTS

The method of presenting results is similar to that employed in previous studies (1). The advancing contact angles are represented by solid symbols and solid curves, whereas the receding contact angles are represented by open symbols and dashed curves.

The contact angle curves are plotted versus percent optical depletion. The optical readings for complete films of myristic and stearic acids formed at pH=6.6 and 18° C differed by about 10% whereas one would expect about a 20% difference for the same molecular packing and percent salt formation. Due to this small difference in optical readings and the small amount of capric acid
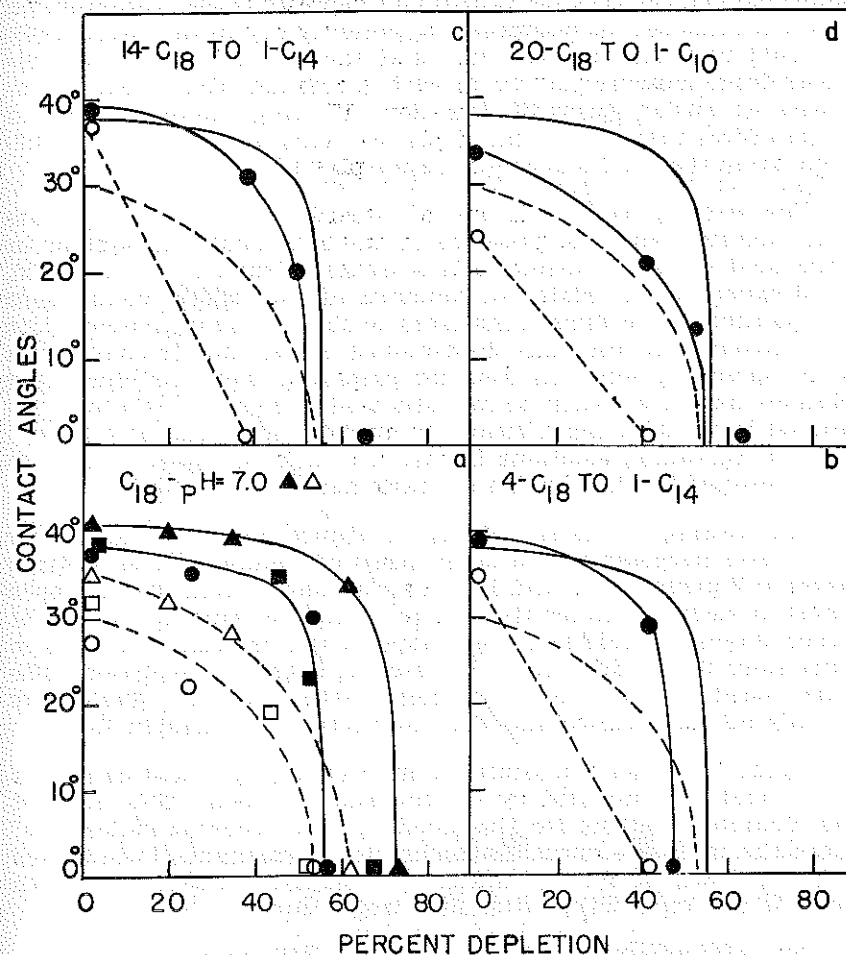

Figure 1. Wetting of complete and mixed films by hexadecane. All measurements at 18° C and pH = 6.6 except the indicated points at pH = 7.0 were at 26° C. The spreading solutions for films were: a. pure stearic acid; b. 1 stearic-1 myristic; c. 4 stearic-1 myristic; d. 1 stearic-5 capric.

in mixed films, no attempt was made to adjust the optical results to reflect the depletion of only one acid in a mixed film. Such minor corrections would lie within experimental variations and would have no significant effect on the interpretation of results.

Figure 1a compares the wetting by hexadecane of a mixed film of stearic acid-barium stearate at pH=7.0 and 26° C with several at pH=6.6 and 18° C. A pH value of 7.0 represents the maximum pH at which films can be withdrawn apparently dry in this system (6). It should be noted that the curves at the pH=6.6 value are displaced from those at pH=7.0 in such a manner that wetting increases at earlier stages of depletion. Wetting curves at higher temperatures than 18° C and at pH=6.6 were not significantly different from the results in Figure 1a for pH=6.6.

The wetting by hexadecane of stearic acid-barium stearate films modified with the presence of small amounts of myristic or capric acid and their barium salts is shown in Figures 1b, 1c, and 1d. In all experimental trials, the amounts of the shorter chain acids incorporated in the films transferred to the chromium-plated slides were considerably less than the amounts of the shorter chain acids in the spreading solutions used for preparing the films. Spreading solutions having a stearic to myristic acid ratio of 1:1, 4:1, and 1:9 resulted in films having a stearic to myristic acid ratio of 4:1, 14:1, and 6:9. Spreading solutions having a stearic to capric acid ratio of 1:5 resulted in films having a stearic acid ratio of 100:5.

The wetting curves at pH=6.6 of Figure 1a are included for comparison purposes in the other trials of Figure 1. The wetting curves in Figures 1b, 1c, and 1d are all displaced from the reference curves in such a manner that more complete wetting occurs at earlier stages of depletion. The shape of the receding curves is in doubt since it was difficult to control the degree of depletion. The initial receding angle and a complete wetting receding angle were the only points obtained and were connected by a straight line.

Figure 1b shows the affect on the wetting by hexadecane of a stearic acid film modified by the inclusion of about 20% myristic acid. Complete wetting for the receding drop occurred at least 15° before the reference curve. Radiochemical measurements indicated that about 40% of the myristic acid molecules were present when complete wetting for the advancing drop occurred.

Figure 1c presents similar results for a film containing initially about 7% myristic acid. Past experience has shown that the indicated precipitous fall of the advancing curve would have been obtained if it were possible to control the depletion process. Radiochemical measurements indicated that about 90% of the myristic acid was removed in the initial depletion and that virtually all of

it was removed by the time that the advancing drop completely wet the film.

Figure 1d shows similar results for a film containing initially about 5% capric acid. The advancing curve is markedly displaced from the reference curve. Small portions of the original receded drops broke away from the bulk of the receded drops and clung to the film. The small value of the initial receding angle reflects this observation. The radiochemical measurements in conjunction with
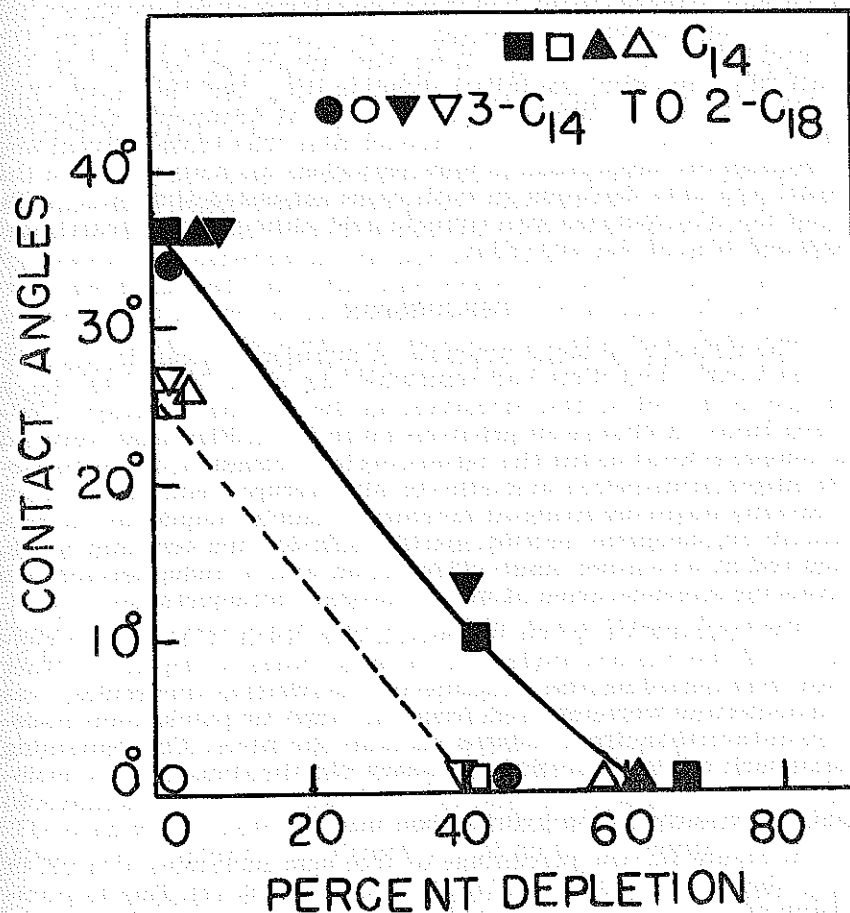

Figure 2. Wetting of complete and mixed films by hexadecane. Measurements at 18° C and pH = 6.6. Spreading solutions for the mixed films were 9 myristic-1 stearic and pure myristic for the unmixed films.

the optical measurements suggested that virtually all of the capric acid was removed in the first depletion.

When myristic acid occupies about 60% of the films, it is more relevant to compare the wetting with complete myristic acid films and this is done in Figure 2. Reference wetting advancing and receding contact angle curves are constructed for several trials for myristic acid films containing no stearic acid and are similar to those previously reported for dodecylamine films (1). The results are also shown for two different films of myristic acid containing about 40% stearic acid. The four experimental points shown for the one film lie within expected experimental deviation from the unmixed myristic acid films as do the advancing angles for the other film. However, the initial receding drop for the latter film completely wet the film although the initial advancing angle was virtually the same as for the reference film. The initial optical and radiochemical measurements were very close for both films and the initial and only depletion in both cases suggested that practically all of the film removed was myristic acid although the stearic acid occupied 40% of the total film.

DISCUSSION

The inclusion of small amounts of myristic and capric acids into the stearic acid films had somewhat the same affect as did a change in the pH of film formation on the wetting behavior of unmixed films. A change in pH from 7.0 to 6.6 in Figure 1a resulted in complete wetting for the advancing and receding drops at earlier stages of depletion and also in the abrupt reduction of the advancing angle occurring at an earlier stage of depletion. In Figures 1b-1d, complete wetting, particularly for the receding angle, occurred at an earlier stage of depletion and a reduction of the advancing angle occurred at an earlier stage of depletion.

The explanation given by Bartell and Ruch (1) for the constancy of the contact angles over a large range of depletion, other than that regarding the structure of the wetting molecules, was that molecules were removed from the edges of patches of molecules rather than from isolated spots in the films. The remaining framework or structure was necessary for the hexadecane molecules to orient in the depleted film and assume a role similar to that of the surrounding hydrocarbon tails.

In Figure 1a, the percentage of free acid molecules at a pH of 7.0 is about 40% and at a pH of 6.6 is about 50% (7). Due to minimizing of repulsive forces, the stearic acid molecules and the barium stearate molecules are probably randomly distributed throughout the film rather than in independent patches. The benzene used for depletion would be a better solvent for the free acid molecules than for the barium stearate. Consequently, upon depletion, there

is a greater possibility of breaking down patches at a pH of 6.6 since there are more of the free acid molecules and more probability of these molecules influencing the structure of the patches. Hence, the ordering would break down more rapidly at the lower pH value and the constancy of the contact angle would break down sooner as shown in Figure 1a.

The above explanation may be extended to the wetting of these films on the inclusion of small amounts of myristic and capric acids. These molecules are most likely randomly distributed throughout the films since upon formation a large percentage of the molecules were lost out of the film on the water surface and only small percentages left in the resultant films. Radiochemical measurements indicated that these shorter chain acids were rather rapidly depleted from the films.

If the short chain molecules occupy the center of patches or clumps as is suggested by Bewig and Zisman (8) for alkane molecules in amine films, then depletion of these molecules would rapidly destroy the ordering in the surface. If the ordering of the films was not destroyed, then the first depletion point in Figures 1b-1d should show larger contact angles since not enough of the stearic acid was removed to lower the advancing angle from the value for the reference film and to give complete wetting for the receding angle.

The results shown in Figure 2 correspond to films where myristic acid was present in large enough quantity in the spreading solution to occupy 60% of the resultant film and stearic acid 40% of the film. One might conceive of the stearic acid molecules occupying some isolated positions in the film or being mainly grouped together in patches. The latter case would seem more likely since registry of the methylene groups would lower the energy of the system. The results of Figure 2 seem to give evidence for each type of film.

In either trial in Figure 2 the initial advancing angle is virtually the same as that for a complete myristic acid film. This can be explained by postulating that the advancing drop will move forward over the surface until the edge of the drop comes to rest on a low energy methyl surface of either stearic or myristic acid areas. The drop would move over the methylene groups exposed by isolated stearic acid molecules and come to rest on lower energy areas.

The behavior of the initial receding angle would be more sensitive to the two cases however. If mostly patches of the molecules exist in the film, the receding drop will move over a somewhat jagged surface but will generally move from one methyl group surface to another and give an angle similar to the complete myristic acid films. If there are stearic acid molecules occupying various

isolated sites in the film, however, the molecules of the receding drop will interact with the dangling tails of the stearic acid and result in a considerable reduction of the receding angle. This, perhaps along with a weakly adsorbed film, may explain why the one film shown in Figure 2 was completely wet by the initial receding drop although the initial advancing angle on the same film was not different from the reference angles.

The observation that parts of the receding drops were left on the film for the stearic-capric trial of Figure 1d may be due to an interaction of the hexadecane with exposed methylene groups. In this case though, the exposed groups may result from hexadecane molecules from the advancing drops having entered holes in the film created by the non-registry of the capric acid molecules with the adjacent stearic acid molecules. Doyle and Ellison (9) proposed that hexadecane molecules can even penetrate between stearic acid molecules with a portion of the hydrocarbon tail extending above the acid film. The capric acid molecules are probably adsorbed on the surface in contrast with the suggestion of Bewig and Zisman (8) that alkanes in such positions in a film do not touch the surface. Since the capric acid occupied only 5% of the film, the effect would not be as pronounced as in the myristic-stearic acid trials in Figure 2. Also, this effect would not be as likely to be noted in Figures 1b and 1c since the voids in the film would lie above the longer myristic acid molecules and the hexadecane molecules would not be as likely to be retained in the holes on receding the drops.

ACKNOWLEDGEMENTS

BIBLIOGRAPHY

1. Bartell, L. S., and Ruch, R. J., J. Phys. Chem., 60, 1231 (1956); Ibid., 63, 1045 (1959).
2. Bigelow, W. C.; Pickett, D. L.; and Zisman, W. A., J. Colloid Sci., 1, 513 (1946).
3. Blodgett, K. B., J. Am. Chem. Soc., 57, 1007 (1935).
4. Wolstenholme, G. A., and Schulman, J. H., Trans. Faraday Soc., 46, 475 (1950).
5. Thomas, J. G. N., and Schulman, J. H., Trans. Faraday Soc., 50, 1128 (1954); Ibid., 50, 1139 (1954).
6. Ruch, R. J., and Tigner, N. L., Proc. S. Dakota Acad. Sci., XL, 194 (1961).
7. Langmuir, I., and Schaefer, V. J., J. Am. Chem. Soc., 58, 284 (1936).

8. Bewig, K. W., and Zisman, W. A., J Phys. Chem., 67, 130 (1963).
9. Doyle, W. P., and Ellison, A. H., "Contact Angle, Wettability, and Adhesion", p. 268, American Chemical Society, Applied Publications, Washington, D. C. (1964).