# Contact Angle Studies on Viable Human Skin: II. Effect of Surfactant Ionic Type in Pretreatment

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## Abstract

The effect of presoaking with various surfactant solutions on the skin-water contact angle was investigated. Various cationic surfactants and amine oxides were found to lower the skin-water contact angle at lowest concentrations. Rinsability data supported the findings and suggested that cationic surfactants are tightly bound to the skin.

## Introduction

The adsorption of surfactants by proteins, for example by keratin, has been noted as being a key property in the application of cosmetics such as skin and hair preparations (1). Adsorbed cationic surfactants give body to fine hair, soften coarse hair, act as lubricants and increase manageability by reducing static. Adsorption on the skin is important in the formulation of barrier creams and numerous other detergent products coming into contact with the skin (2). As with other substrates, the degree of adsorption on biological substrates depends on the condition of the surface, the cationic chemical type, the solution concentration, pH and temperature. The bactericidal properties of cationic surfactants are widely employed in various consumer applications, including antiperspirants, deodorants, antiseptic creams and lotions, dandruff remedies, and various oral preparations.

The adsorption of surface active agents on living human skin has received little clarification because of the lack of quantitative data and the experimental difficulties involved. Recently, workers in our laboratories developed a new contact angle technique to detect and characterize films on living skin tissue (2). The simple technique involves placing droplets of water on the dorsal side of the index finger and measuring the angle of contact with a telescope goniometer. The skin-water contact angle was found to be sensitive to the condition or pretreatment of the skin. It was noted that clean and degreased skin gave a high contact angle with water (>100°) and behaved like a hydrophobic surface (similar to polyethylene or polypropylene). The critical surface tension for wetting clean skin was found to be 26.8 dynes/cm. Using our technique, Adamson et al. have confirmed these findings (3). The contact angle of clean skin was found to be reduced by the presence of minute quantities of surface active agents on the skin, and particularly by hydrophilic substances. This work suggested that contact angle measurements could be used as a sensitive tool for detecting surfactant interactions with the skin.

## Experimental Procedures

The basic techniques employed are given in reference (2). This procedure has been applied in measuring the skin-water contact angle after soaking the skin in aqueous surfactant solutions at known concentrations. It makes it possible to estimate the desired surfactant concentration necessary to achieve optimum skin substantivity, and particularly for hydrophilic residues (low contact angles). The rinsability study, which follows the soaking test, measures the removability of the surfactant after it is sorbed by the skin. Rinsability data therefore complement soaking data in assessing the substantivity of a given surfactant system. Precision of contact angles = ±5° (95% confidence limits).

### Equipment and Materials

NLR Contact-Angle Goniometer Model A-100; hydrodermic syringe with fine needle; watch with second hand; deionized water; 150 ml beakers; constant temperature water bath (110 ± 0.5 F); ethyl alcohol-deionized water (95:5).

### Procedures

*Preparation of the Test Solutions.* A 1% stock solution of the sample in a 1000 ml volumetric flask, brought to volume with deionized water, was prepared. Using the 1% stock solution, a 0.5% solution in a 500 ml volumetric flask was prepared. The 0.5% solution was transferred into a 800 ml beaker and placed in the constant temperature water bath at 110 F.

*Skin Treatment.* The hands were cleansed by washing thoroughly with a 75:25 tallow-coconut fatty acid soap bar (no additives). After washing, the hands were rinsed with tap water, followed by rinsing with deionized water. The index and the middle finger were both dipped five consecutive times in 150 ml of the 95% ethanol solution. Rinsing, first with tap water and then with deionized water followed. The fingers were allowed to air dry.

*Measurement of Contact Angle.* The goniometer was adjusted as in Reference 2. Using the microsyringe, three small drops (about 1–3 μliters) of deionized water were placed on the index finger and three drops on the middle finger of the left hand. After 90 sec, the contact angle from the goniometer scale at the index line was read. This was done after turning the outer goniometer dial so that the crosshair was tangent to the left side of the drop where the drop touched the skin. If the contact angle measured was lower than 110 F the skin pretreatment was repeated.

*Soaking Procedure.* The left hand was soaked for 10 min in the 0.5% solution which was contained in the water bath at 100 F. After soaking, the hand was rinsed by dipping two consecutive times in a 1000 ml beaker of 105 F water. The beaker was refilled and the water rinse repeated. The hand was air dried. The contact angle was measured as noted above. The testing of solutions of decreasing concentration was continued until the water-skin contact angle was greater than 100 F. The concentrations generally used were 0.10%, 0.05%, 0.02%, 0.01%, 0.005% and 0.001%.

*Rinsability.* A 0.2% solution (500 ml) from the stock solution was prepared and placed in the con-

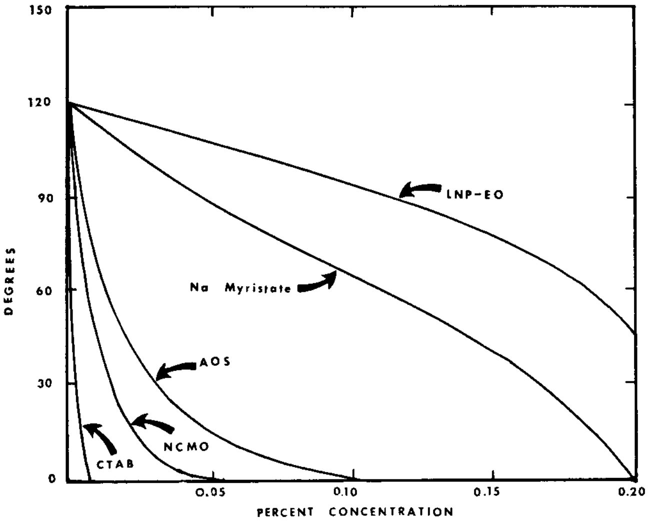

FIG. 1. Contact angle reduction by surfactants. LNP-EO, ethoxylated nonylphenol 9 E.O.; AOS, alpha olefin sulfonate (commercial mixture); NCMO, N-cocoalkylmorpholine oxide; and CTAB, cetyltrimethylammonium bromide.

stant temperature water bath at 110 F. The skin was cleaned as in the pretreatment procedure above and the skin-water contact angle was checked. The soaking procedure was repeated as above, but the 0.2% solution for soaking was used. The hand was rinsed by dipping two times in 1000 ml of 105 F water. The contact angle was read after the hand was air dried. The beaker was refilled and the water rinsing and drying followed by contact angle measurement was repeated. The rinsing and measurement cycles to a total of 16 hand dippings were also repeated.

## Results and Discussion

Figure 1 shows the curves obtained which relate the skin-water contact angle to the surfactant concentration in the soak solution. The effectiveness of the cationic agent in reducing the contact angle is evident from this graph. Cationics reduced the skin-water contact angle to zero at soak concentrations as low as 0.0025% to 0.005% by weight.

Results given in Table I compare various cationics and amine oxides in ability to reduce the skin-water contact angle. Listed are the soak concentrations, expressed as molarity, required to reduce the angle to 60. Cationics tend to be effective at $10^{-5}$ molar concentrations and amine oxides at $10^{-4}$ molar concentrations.

Table II shows results for some of the anionic agents tested. It is evident that higher concentrations of these compounds are required, that is, 1 to 3 orders of magnitude higher than the amine oxides. The more effective of these compounds were sodium tridecylbenzenesulfonate and an alcohol ethoxysulfate. Alpha olefin sulfonates gave variable results depending on the proportion of hydroxyalkylsulfonates present in the samples.

TABLE I

| Code | Surfactant | Molarity for 60° Angle |
|---|---|---|
| TDTAB | Tetradecyltrimethylammonium bromide | $3.0 \times 10^{-5}$ |
| CTAB | Cetyltrimethylammonium bromide | $5.0 \times 10^{-5}$ |
| DMTDAO | Dimethyl(tetradecyl)amine oxide | $2.0 \times 10^{-4}$ |
| NCMO | N-Cocoalkyl morpholine oxide | $1.4 \times 10^{-4}$ |
| NTDMO | N-Tetradecyl morpholine oxide | $4.0 \times 10^{-4}$ |

TABLE II

| Code | Surfactant | Molarity for 60° Angle |
|---|---|---|
| LAS-12 | Sodium dodecylbenzenesulfonate | $4.3 \times 10^{-3}$ |
| LAS-13 | Sodium tridecylbenzenesulfonate | $8.4 \times 10^{-4}$ |
| AOS | Alpha olefin sulfonate | $0.3–3.0 \times 10^{-3}$ |
| AES | $NH_4$ N-$C_{12}$-$C_{14}$ Alcohol-3EO sulfate | $7.0 \times 10^{-4}$ |
| $C_{12}$ Soap | Sodium laurate | $1.4 \times 10^{-2}$ |
| $C_{14}$ Soap | Sodium myristate | $2.0 \times 10^{-3}$ |
| $R_{12}OSO_3$ | Sodium N-dodecyl sulfate | $9.0 \times 10^{-3}$ |
| $R_{18}OSO_3$ | Sodium N-octadecyl sulfate | $1.3 \times 10^{-3}$ |

Experiments were conducted to determine the ease with which various compounds could be removed from the skin by further rinsing with deionized water. The data just discussed were obtained after rinsing the skin four times with deionized water. To derive rinsability data, skin treated with 0.2% surfactant soak concentrations was measured. Skin was measured after further rinsing, that is, after 8, 12 and 16 rinses (Fig. 2). This technique provides a measure of the tenacity with which the surfactant is held by the skin. Thus, a compound which tends to reduce the skin-water contact angle to zero, at very low soak concentrations, would be expected to give relatively lower angles than other compounds, even upon additional rinsing. This figure shows that this is the case and, with but few exceptions, the compounds tending to reduce contact angles to the greatest extent were least affected by subsequent rinsing. The cationic, cetyltrimethylammonium bromide, and the amine oxide, N-cocomorpholine oxide, yielded zero skin-water contact angles even after 16 rinses. These compounds may be considered rather strongly bound to the skin. It appears that the contact angle lowering may be interpreted as a rough measure of substantivity, although other factors are operating, such as extractability or diffusion into the water droplet, surface activity in the water droplet, orientation on the skin, etc. Sodium myristate yielded zero contact angle after eight rinses, but further rinsing apparently removed this compound quite rapidly from the skin. The alpha olefin sulfonate and the non-

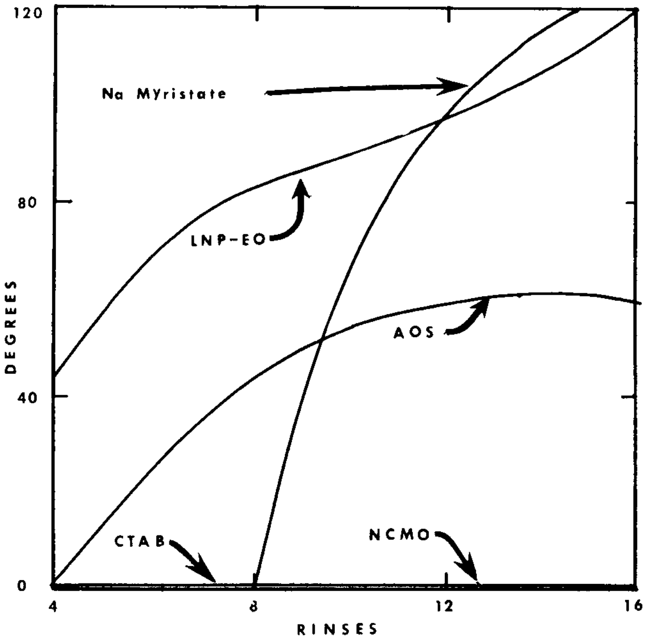

FIG. 2. Rinsability studies.

TABLE III

| Classification | Agent |
|---|---|
| Highest in effect | Cationics<br>Amine oxides |
| Intermediate in effect | Alkylbenzenesulfonates<br>Alpha olefin sulfonates<br>Alcohol ethoxy sulfates<br>Soaps<br>Alcohol sulfates |
| Lowest in effect | Nonionic ethoxylates<br>Alkenyl sulfonates<br>Alkane sulfonates |

ionic surfactant seemed to come off the skin more gradually and seem less tenaciously bound.

While the skin-water contact angle is an indirect measure of substantivity, and other variables are operating simultaneously, it was possible to rank surfactants according to their order of effectiveness. Table III gives the rough order effectiveness based on the data gathered to date. Highest in effect were cationic surfactants and amine oxides. Considerably lower in effectiveness were various anionic and nonionic surfactants.

According to Idson (4), human skin acts as an ion exchange membrane which absorbs charged ions on its amphoteric protein surface. Oils are attracted to the skin by weaker van der Waals bonding while surfactants bind according to size and charge of the cation or anion. Because of the combination of surface activity and strong adsorption, cationic surfactants are powerful antiseptics.

The outer surface of the skin is a complex matrix of proteins, water soluble components, and lipids. Keratin contains large proportions of acidic and basic groups (5). As with more simple proteins, it would be anticipated that reactivity of surfactants with human skin would depend on the pH of the aqueous media. Considering, by analogy, the various amino acids found as terminal groups of wool protein, it may be assumed that at neutral pH, the skin surface would be above its isoelectric point. Adsorption of cationics from neutral solutions would therefore be expected to occur to a greater extent than adsorption of other surfactant ionic types by skin (6). The experimental findings presented in this paper tend to support this view.

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