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The interaction between surfactants and keratinous tissues

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Synopsis

During cosmetic treatments, SURFACTANTS penetrate into KERATINOUS TISSUES (hair, skin and nails). Whereas some of these surfactant molecules migrate to the vital tissues, a considerable fraction remains bound to the keratin. The extent of binding depends both on the nature of the head group and the length of the hydrophobic tail of the detergent molecules. In addition to entering the amorphous region of the keratin, some of the detergents also penetrate into the crystalline microfibrils and change their structures affecting their tensile properties. Owing to an uneven distribution of detergent molecules in the tissues, an anisotropy of the elastic moduli will occur, resulting in considerable internal stresses which, in turn, might lead to a deterioration of hair, skin and nails. The chemical behavior of keratins is also influenced by the presence of absorbed detergent in their structures. Depending on the detergents and the conditions, these effects can be either protective or detrimental. The deposition of detergent molecules into keratin can be enhanced or diminished by the inclusion of appropriate ingredients into the product formulae.

I. INTRODUCTION

Surfactants come into daily contact with human keratinous tissues (hair, skin and nails). As a result of these exposures, a fraction of the surfactant molecules will reach, after penetrating and migrating through the keratinous tissues, the vital layers of the skin (e.g., migrate through the stratum corneum or nails and penetrate the epidermis and the dermis) and will eventually enter the blood stream. The bulk of the penetrating molecules, however, will remain bound to the keratin structure itself. The various physicochemical factors governing the penetration and migration of surfactants in skin and the biological responses which the presence of these surfactants in the living tissues evoke, have been extensively studied and reported in the past (1). On the other hand, no critical literature review exists that surveys the binding of surfactants to keratins and the effects which the presence of the surfactants in the keratinous tissues exert on the physical and the chemical properties of hair, skin and nails. This void in our knowledge is regrettable, especially as many of the important cosmetic attributes of skin, hair and nail depend on the physical and chemical integrity of their constituent

keratins. The present communication aims to fill this gap and intends to review critically the current knowledge, as it appears in the published literature, on these subjects. In attempting this task, it is necessary to make the assumption that the experimental data obtained on keratins from different origins (e.g., hair, wool, mohair, stratum corneum, etc.) are interchangeable and, thus, can be pooled. In view of the known chemical differences between the various keratins, this assumption cannot be regarded as being completely correct. Nevertheless, it is the author's view that the errors committed by the pooling of data obtained from keratins of diverse origins affects only the quantitative aspects of the conclusions and does not influence the essential features of our understanding regarding the effects of surfactants on the cosmetically important properties of keratins.

II. THE UPTAKE OF SURFACTANTS BY KERATINS

Essentially the magnitudes of two quantities determine the extent of a binding of surfactants to a keratinous tissue: n_∞ the maximum nuber of molecules that the keratin in question can accommodate, and Δ G, the free energy change (i.e., the affinity) that

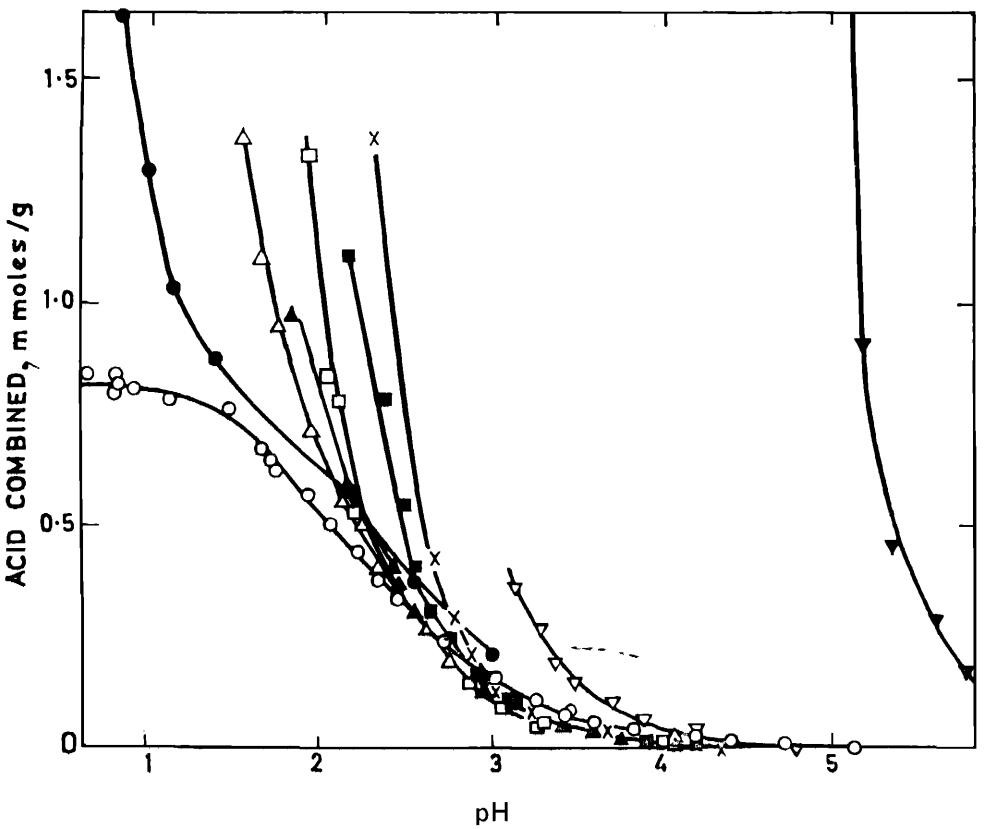

Figure 1. Uptake of acids by wool keratin. Acids: ○ Hydrochloric, ● dichloroacetic, Δ Monochloracetic, formic, □ glycolic, ■ acetic, X propionic, ▽ benzoic, ▼ p-nitrophenol. (Reproduced with permission from reference 3.)

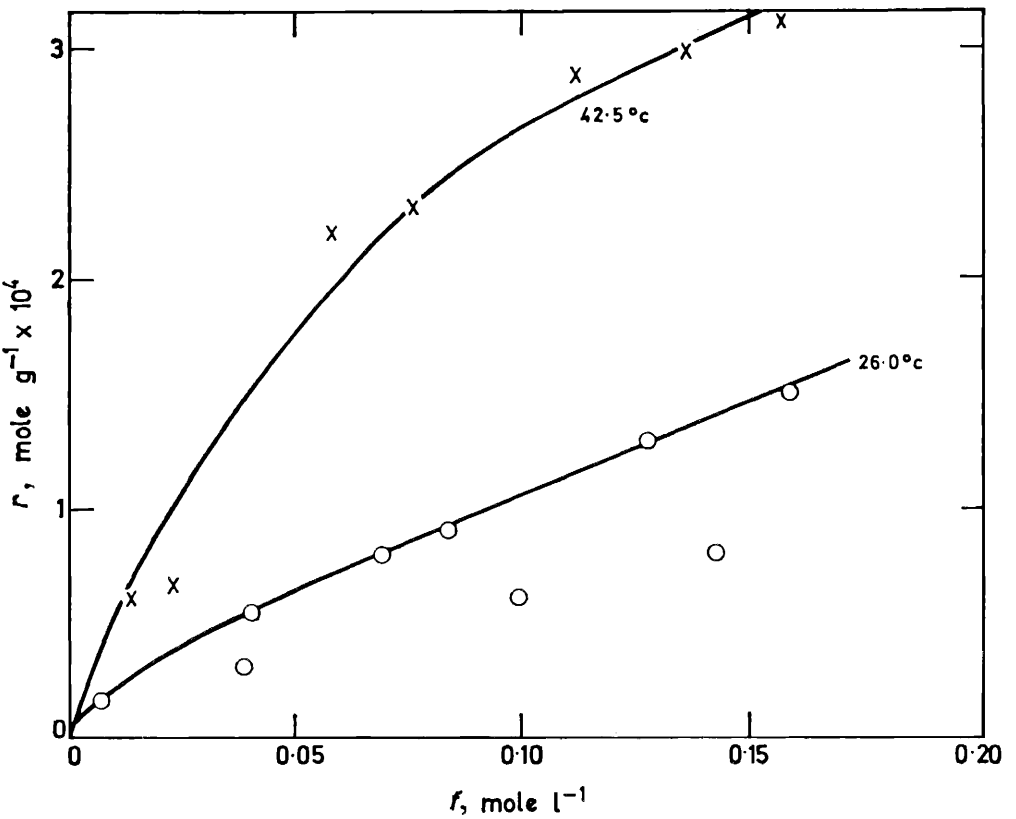

Figure 2. Binding isotherms of sodium naphthalene sulphonic acid to human hair; f and r denote the equilibrium concentrations and the uptakes, respectively. (Reproduced with permission from reference 3.)

characterizes the absorption processes and, thus, measures the strength of the binding. Two types of experimental approaches have been used for the determination of these quantities in the past. In the 1940s Steinhardt, Fuggit and Harris measured the uptake of many acids and bases by wool using potentiometric titration (2). From the plateau regions of the titration curves at extreme pH values, these authors determined the maximum binding capacity of wool towards the various acids (Figure 1). The mid-points of the titration curves, i.e., the pH values at which half saturation occurred, served as the basis for calculating the affinities of the acids to the wool. More recently (3,4), a different experimental approach was pursued for measuring uptakes of materials by hair and other keratins. In this technique the levels of binding were determined as a function of the concentration of the absorbate in solution at a constant pH value. Generally, reciprocal plots were also prepared from the binding data as these allowed a more accurate extrapolation to infinite concentrations and, therefore, a more precise determination of the binding capacities of the absorbants (3). (For typical isotherms, see Figures 2 and 3.) The binding free energies could be obtained from the absorption isotherms by a variety of mathematical techniques (4,5).

The experimental data from these types of studies led to a number of important conclusions (3). Firstly, it appeared that, at given pH and molar concentration, charged compounds were taken up by keratins to a much lesser extent than their uncharged

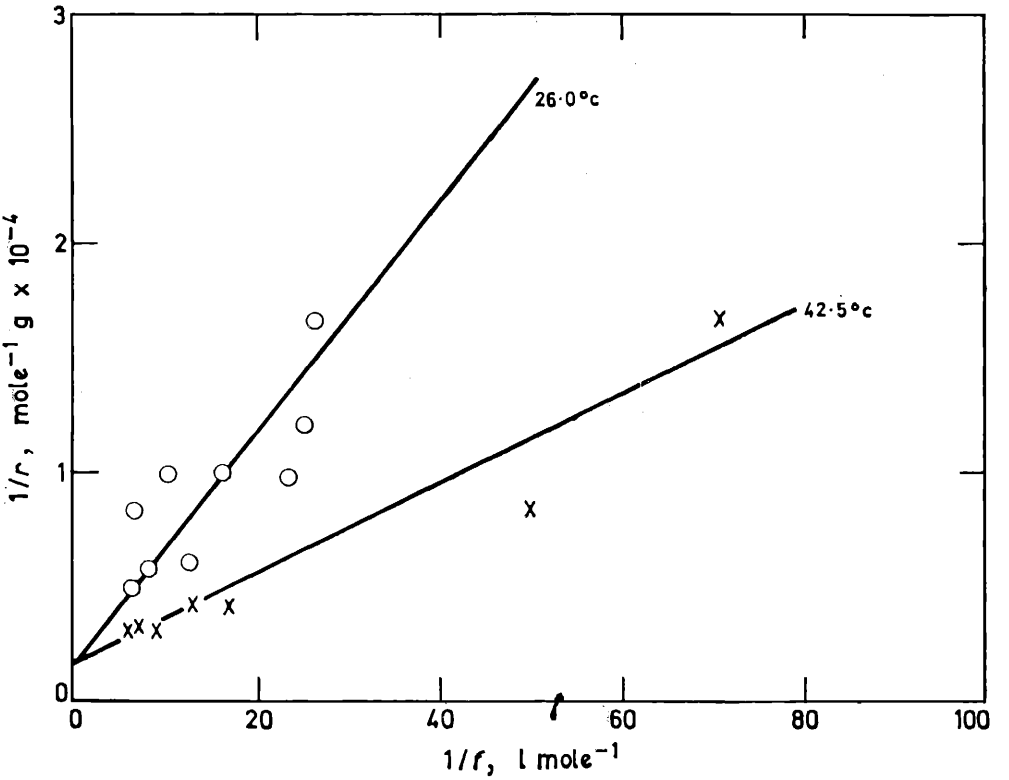

Figure 3. Reciprocal plots of the binding isotherms of sodium naphthalene sulphonic acid; f and r denote the equilibrium concentrations and the uptakes, respectively. (Reproduced with permission from reference 3.)

counterparts, i.e., molecules of similar sizes and shapes. In fact, it did not seem to matter whether the charges on the molecules were only of one type (i.e., either positive or negative) or whether the molecules carried both types of charges attached to their structures (i.e., zwitterions). In either case, strongly diminished uptakes were observed compared to those obtained with uncharged molecules of similar sizes (Table I).

Table I
Uptake of Various Organic Compounds by Virgin Hair

	Uptake mol/g
Phenol	2.8×10^{-4}
Resorcinol	3.0×10^{-4}
Catechol	2.9×10^{-4}
Hydroquinone	1.8×10^{-4}
1,3 Dihydroxy-naphthalene	8.0×10^{-4}
Sodium benzene sulphonate	0.05×10^{-4}
Sodium naphthalene sulphonate	0.80×10^{-4}
Sodium picrate	0.18×10^{-4}
Trimethylamine-benzimide	0.05×10^{-4}
Trimethylamine-naphthimide	0.05×10^{-4}

All uptake values were taken at pH 6, 25°C and at equilibrium concentration 0.04 mol/l. (Data reproduced from reference 3.)

Table II
Binding Constant of Various Substances To Wool and Bovine Serum Albumine (BSA)

Substance	MW	−log K Wool	BSA
Acetone	63	0.39	2.84
Dinitrophenol	184	1.69	5.27
Na Picrate	229	2.63	5.27
Naphthalene Sulphonic Acid	194	2.56	4.69
Octyl Sulphate	194	2.56	6.47
Dodecyl Sulphate	266	3.33	6.77
Orange II	328	4.27	5.35

Sources: Wool data reference 5. BSA data reference 4.

A closer examination of the affinities (i.e., the free energy changes accompanying the binding processes of various materials to keratins) also revealed some interesting features. In Table II the logarithms of the respective binding constants of a series of materials to wool and to bovine serum albumin (BSA) are tabulated and compared. The same data are also shown in Figure 4 as a function of the molecular weights of the compounds. The binding free energies of substances to keratin were substantially

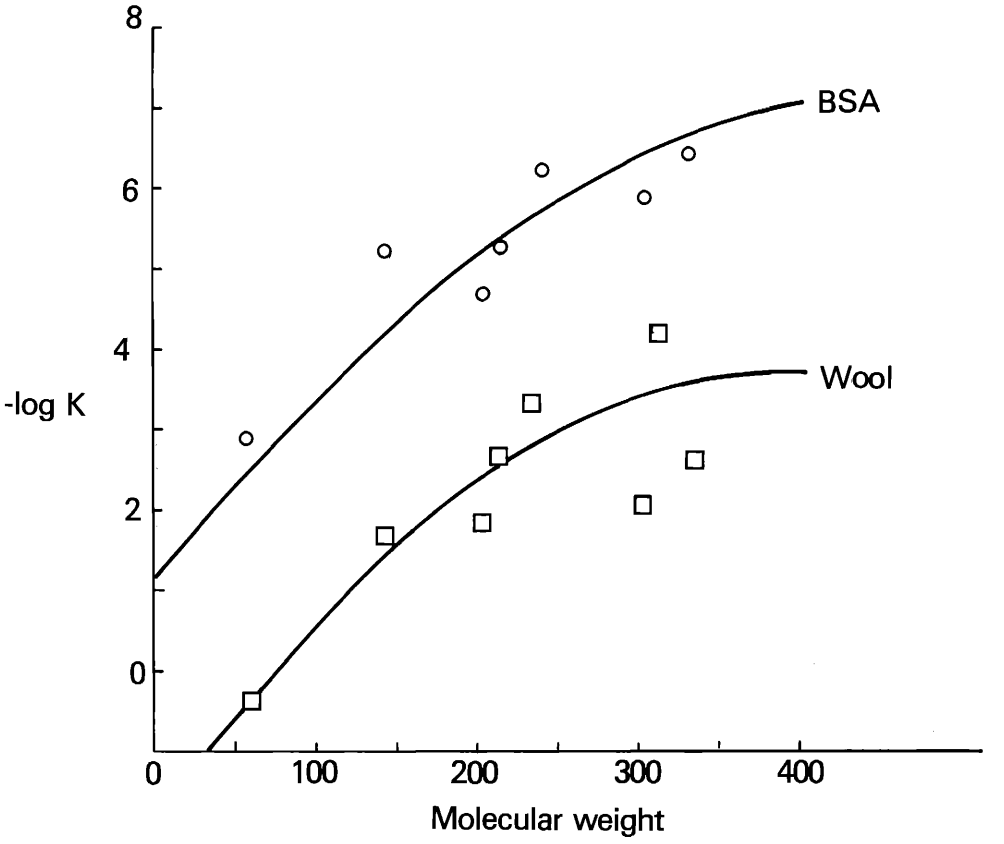

Figure 4. The binding constants of various materials on BSA and Wool as functions of their molecular weights.

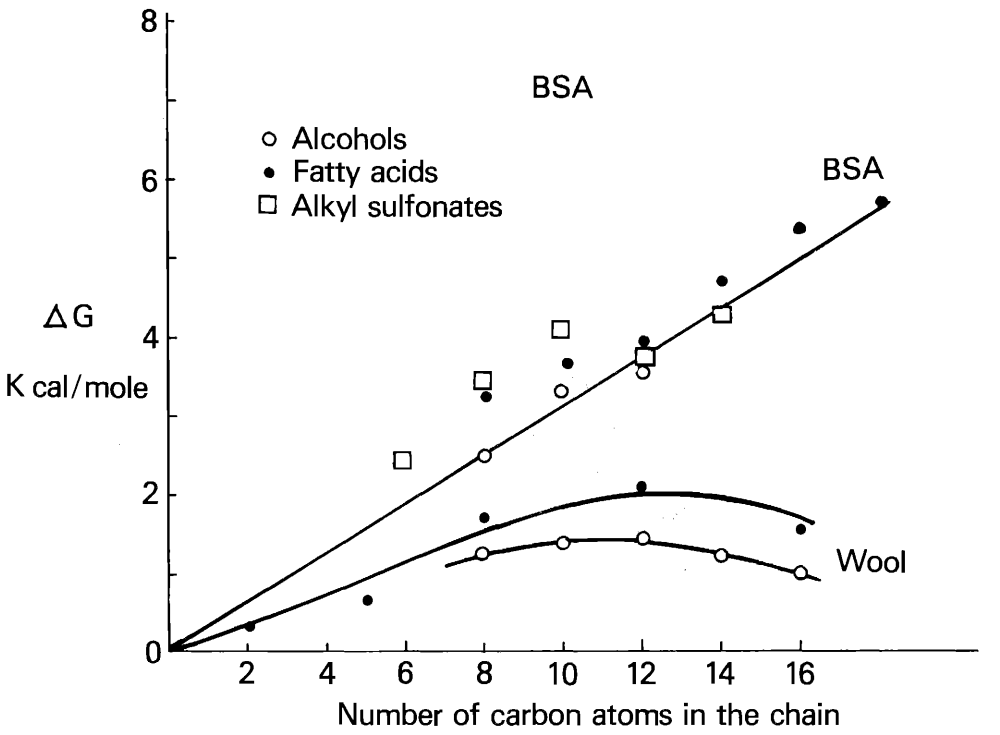

Figure 5. The free energy changes accompanying the adsorption of aliphatic materials as a function of their carbon chain length. (Data obtained from references 4 and 5.)

lower than those of the same compounds to BSA. Differences were also observed when the free energies of absorption of various homologous aliphatic compounds were plotted as functions of their chain lengths, i.e., the number of carbon atoms in the aliphatic chain (Figure 5). The free energy values showed a steady increase in the case of BSA, but reached a maximum around 12 carbon atoms in the case of keratin. For the same type of compounds, the absolute values of the free energy changes were considerably lower in the case of wool than those measured for BSA. In order to understand these results and, in particular, the differences in behavior between the binding free energies to keratins and soluble proteins (e.g., BSA), it is necessary to consider first the structure of keratin. Among the many structural models postulated for keratins (for a review of the various models see ref 6) the one that regards keratin as a partially crystalline crosslinked, polyelectrolyte gel appears the most suitable for our discussions (7). A schematic representation is given in Figure 6. Attached to the main polypeptide chains are positive and negative ionic groups and hydrophobic side chains, all of which may act as binding sites for charged compounds with hydrophobic tails. In general, when surfactant molecules come into contact with a protein, the ionic part of the surfactant interacts with an oppositely charged group attached to the protein structure to form an ion pair (4). On the other hand, the nonpolar tail of a surfactant seeks out a hydrophobic region of the protein to form a hydrophobic bond (4, 8). As a result, the overall binding free energies of surfactants to keratin are sums of two terms corresponding to the electrostatic and nonpolar interactions, respectively. We know that hydrophobic interactions are proportional to the length of the hydrocarbon chains

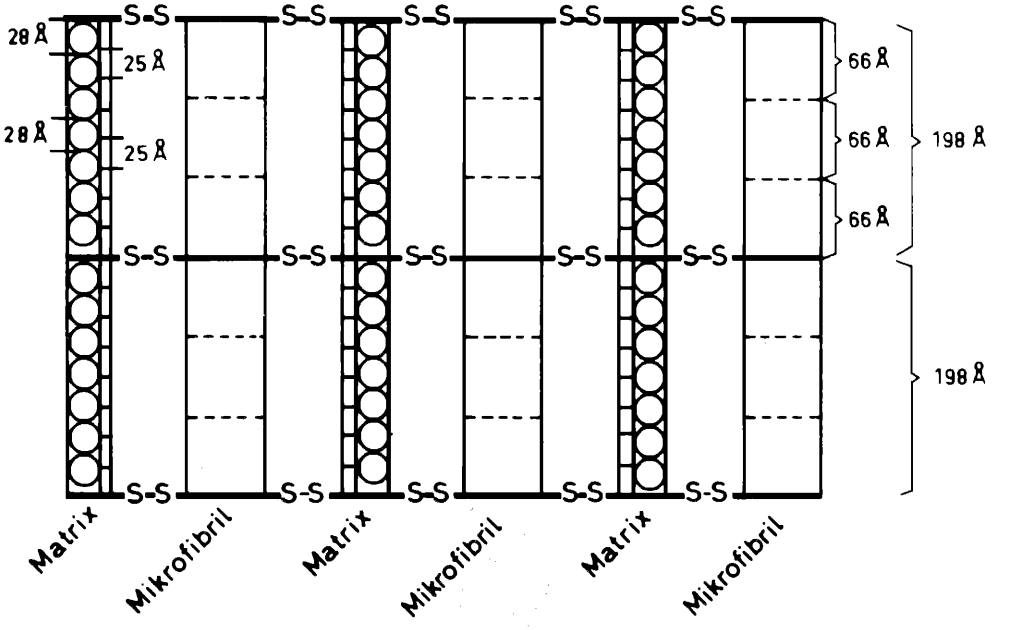

Figure 6 Model proposed for the keratin structure; keratin consists of three ordered components—one microfibrillar component and two matrix components. (Reproduced with permission from reference 7.)

which come into contact with each other (8). The binding energies of detergents to proteins, therefore, can be expected to increase linearly with the length of the hydrophobic chain, as observed experimentally in the case of bovine serum albumin (Figure 5). With keratin, however, an additional factor also affects the binding characteristics of surfactants. Keratins, as mentioned before, are highly cross-linked polypeptide gels. To penetrate into a cross-linked structure of this type, the surfactant molecule has to pry apart the constituent chains, i.e., to overcome the elastic energy of the polypeptide network. The work required to accomplish this will be proportional to the volume of the penetrant molecule. Consequently, the larger the surfactant molecule, the more difficult will be the penetration of the keratin structure and the interaction with the various binding sites attached to the protein chains in the interior of the tissues. The differences between the respective free energies of binding of surfactant molecules to BSA and to keratin are measures of the additional thermodynamic work that is required for the surfactant molecule to reach the binding site in the keratin structure. This model also accounts for the turndown of the free-energy-vs.-carbon-chain-length curve in the case of keratin for molecules with aliphatic chains longer than C_{12} (Figure 5).

III. THE ROLE OF CHARGE IN BINDING OF SURFACTANTS TO KERATINS

As mentioned before, it is an experimental observation that charged compounds penetrate keratinous tissues to a much lesser extent than do uncharged molecules of similar sizes. The presence of cross-links in keratin structure is unlikely to account for this negative effect of charge. To explain it, therefore, we have to consider the

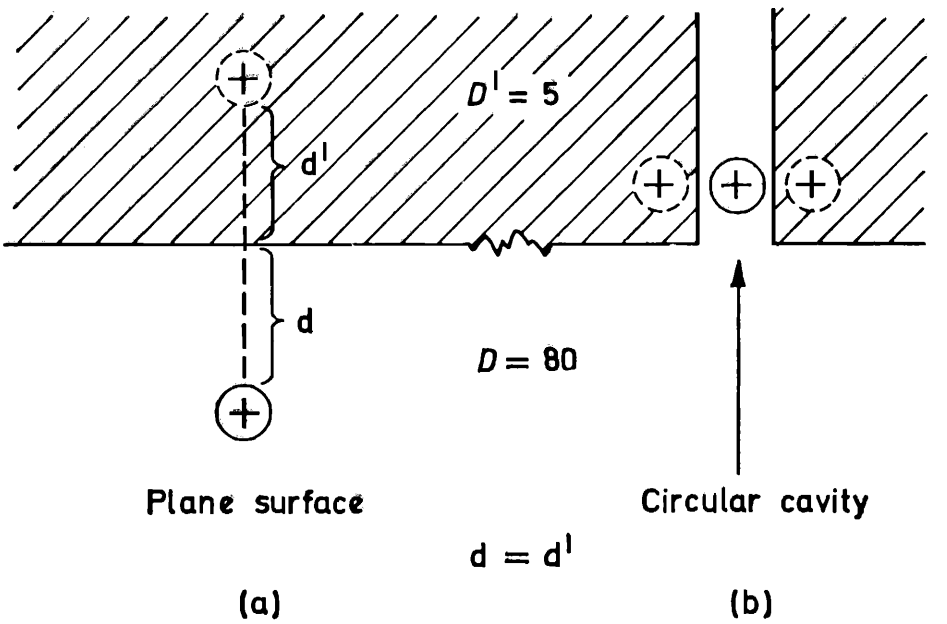

Figure 7. Schematic representation of ions at protein-water interfaces. (a) Ion at a plane interface. (b) Ion in a circular cavity. D, D′, d and d′ denote the dielectic constant of water and protein and the distances of the floating and fixed ion mirror images from the interface, respectively. (Reproduced with permission from reference 3.)

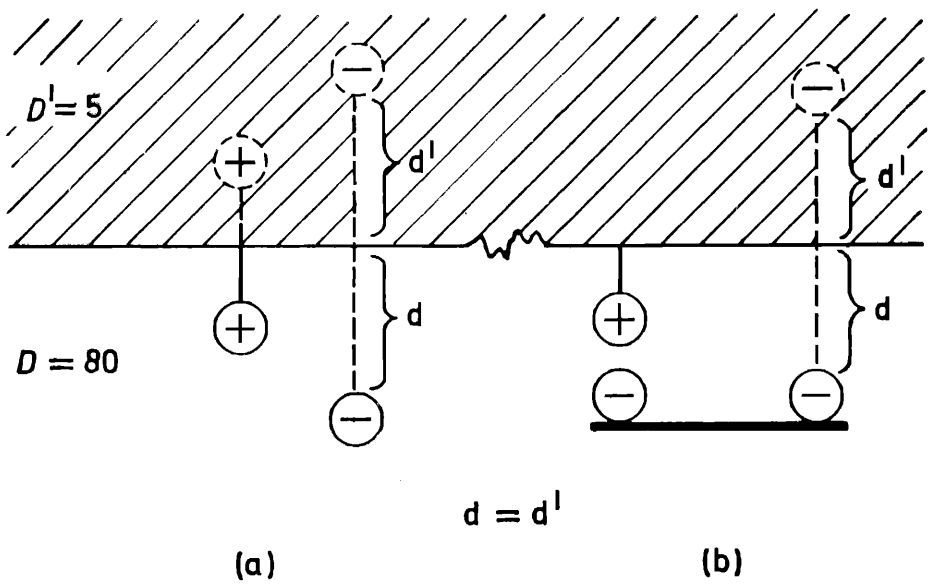

Figure 8. Schematic representation of ions interacting with a fixed charged site situated at a protein-water interface. (a) Interaction of a monovalent dye with a charged site. (b) Interaction of a divalent dye with a single charged site. (Reproduced with permission from reference 3.)

electrostatics of the processes that occur when a freely floating ion in water (i.e., in a high dialectic constant medium) approaches an interface with a low dielectric constant medium such as a protein. According to electrostatic theory, an electric charge embedded in a high dielectric constant medium induces a repulsive force as it approaches an interface with a low dielectric constant continuum. The magnitude of this repulsive force can be calculated by assuming that a mirror image of the approaching ion exists on the other side of the interface (Figure 7). Using simple coulombic calculations, the repulsive electrostatic energy can be obtained from this type of model. This electrostatic repulsion of the mirror images is generally sufficient to overcome the attractive hydrophobic bonds and is sufficient to prevent the binding of an ionic species to a binding site that does not have a fixed oppositely charged ionic component (3). The situation is different, however, when the binding side is composed of a fixed charge with a hydrophobic region around it. In this case, the mirror image forces of the fixed charge and of the floating charge will cancel out and binding of the surfactant molecule with take place (Figure 8). Further verification for the mirror image effect as a reason for preventing the binding of charged species to proteins on noncharged sites, can also be obtained by examining the binding of divalent ions to proteins. Contrary to what is expected on the grounds of electrostatic attraction, it was found that a divalent ion will bind to a lesser extent to a protein than a monovalent ion of a similar structure and size. Medley (9) compared the titration curves of two dyes, Acid Orange 7 and Acid Orange 10, the structures of which only differed in as far as one of the dyes contained an additional sulfonic group attached to its molecular skeleton. (For formulae see Figure 9.) For the same dye concentration and pH, th divalent dye showed a lower uptake on wool than the monovalent species, in agreement with the theoretical predictions based on mirror image repulsion theory (Figure 10). In conclusion, it can be stated that both theoretical considerations and the experimental results indicate that charged surfactant molecules, unless bound by an oppositely charged group of the protein, have more difficulties in penetrating keratins than their uncharged counterparts.

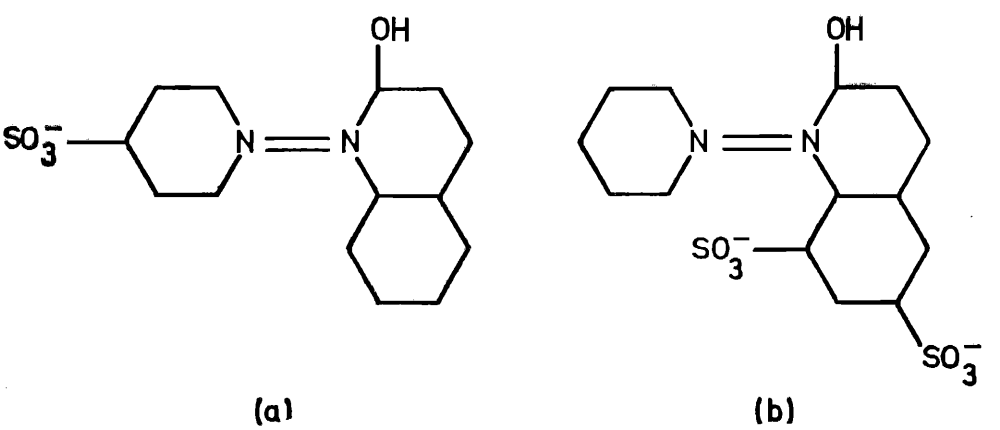

Figure 9. Formulae of Acid Orange 7 and Acid Orange 10. (a) C.I. Acid Orange 7 Naphthalene Orange G, or N.O.G. (b) C.I. Acid Orange 10 Napthalene Orange 2GS, or 2GS. (Reproduced with permission from reference 9.)

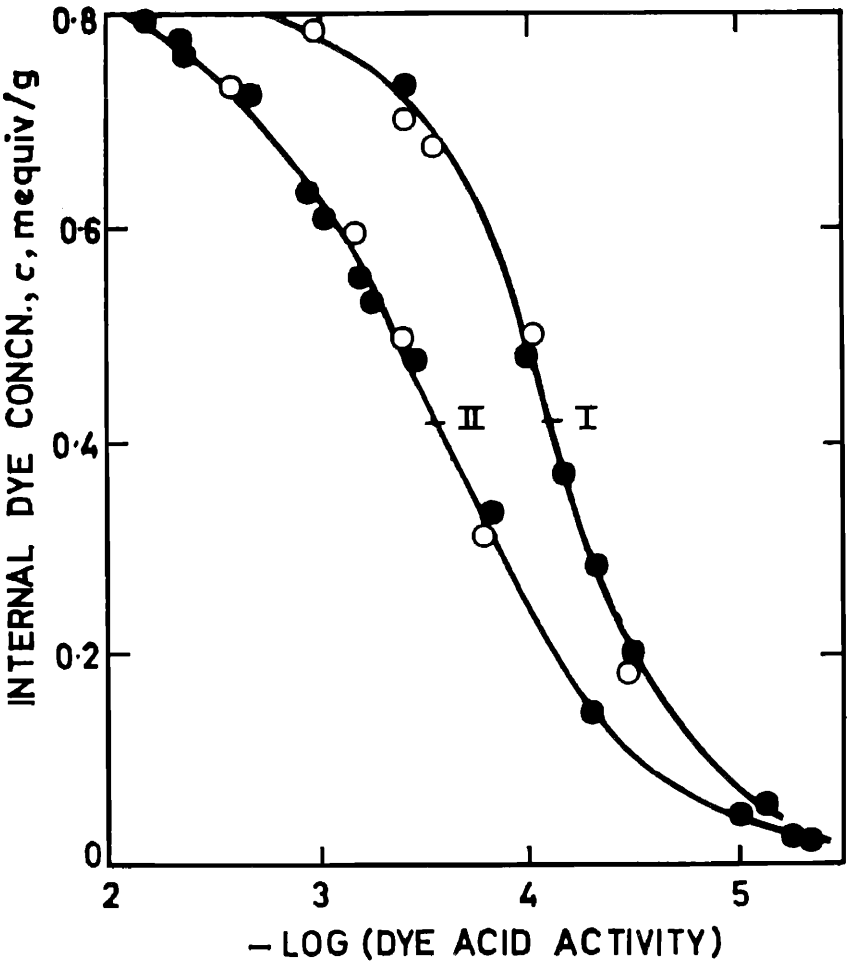

Figure 10. Titration curves of keratin with Acid Orange 7 (I) and Acid Orange 10 (II). (Reproduced with permission from reference 9.)

IV. THE ROLE OF THE DIFFUSION PROCESSES IN DETERGENT-KERATIN INTERACTIONS

The previous sections dealt with the uptake of detergents by keratins essentially from a thermodynamic point of view, i.e., it attempted to define the factors governing the uptakes at equilibria after exposures of very long times. When discussing effects of detergents under practical treatment conditions however, the rates of the surfactant uptake processes also become important. Since cosmetic treatments are generally of relatively short durations, i.e., last about 10–15 min, the detergents absorbed in the tissues will not reach a uniform, equilibrium distribution by the end of the treatment time. On the contrary, in most instances sharp concentration gradients of the surfactants will exist with the high values of concentration near the tissue surfaces exposed to the treatment solutions. As we shall discuss in the following sections of the paper, the properties of the keratinous tissues depend not only on the total amounts of surfactants present, but also on their spatial distribution which is determined by the

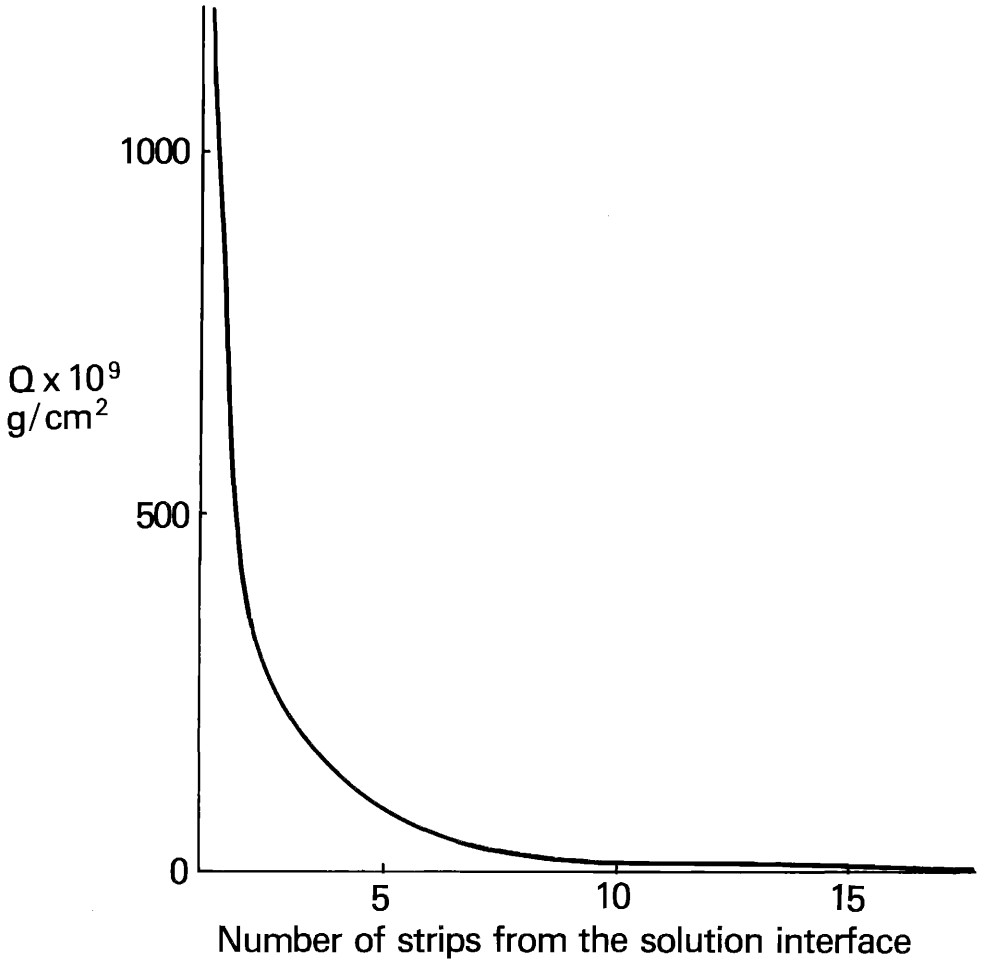

Figure 11. Sodium dodecyl sulfate (SDS) content of strips of isolated stratum corneum after limited exposure to SDS solution. (Reproduced with permission from reference 10.)

rate of migration of the material in question. Unlike the equilibrium uptakes, the diffusion coefficients of charged and uncharged materials are very similar in magnitudes and are about four order of magnitude lower than those of the same compounds in water (3). The relatively low values of the diffusion coefficients cause highly asymmetrical distributions of the penetrating materials in the keratinous tissues during short exposure times. Poret (10) has studied the distributions of sodium lauryl sulfate and of capryl monoglyceride in vitro, using isolated stratum corneum and, in vivo, using guinea pigs, during relatively short exposure times. Exposing stratum corneum samples to C^{14} labeled compounds and stripping layer after layer, he found that the concentration of both these penetrants decreased rapidly with the distance from the solution skin interface (Figure 11). It is interesting to note that the normalized concentrations of both these substances, i.e., the actual concentrations divided by the respective contents of the second strips, were identical with experimental error (Figure 12), confirming again the previous findings that the diffusion coefficients of the various substances in keratins are, to a good approximation, independent of the

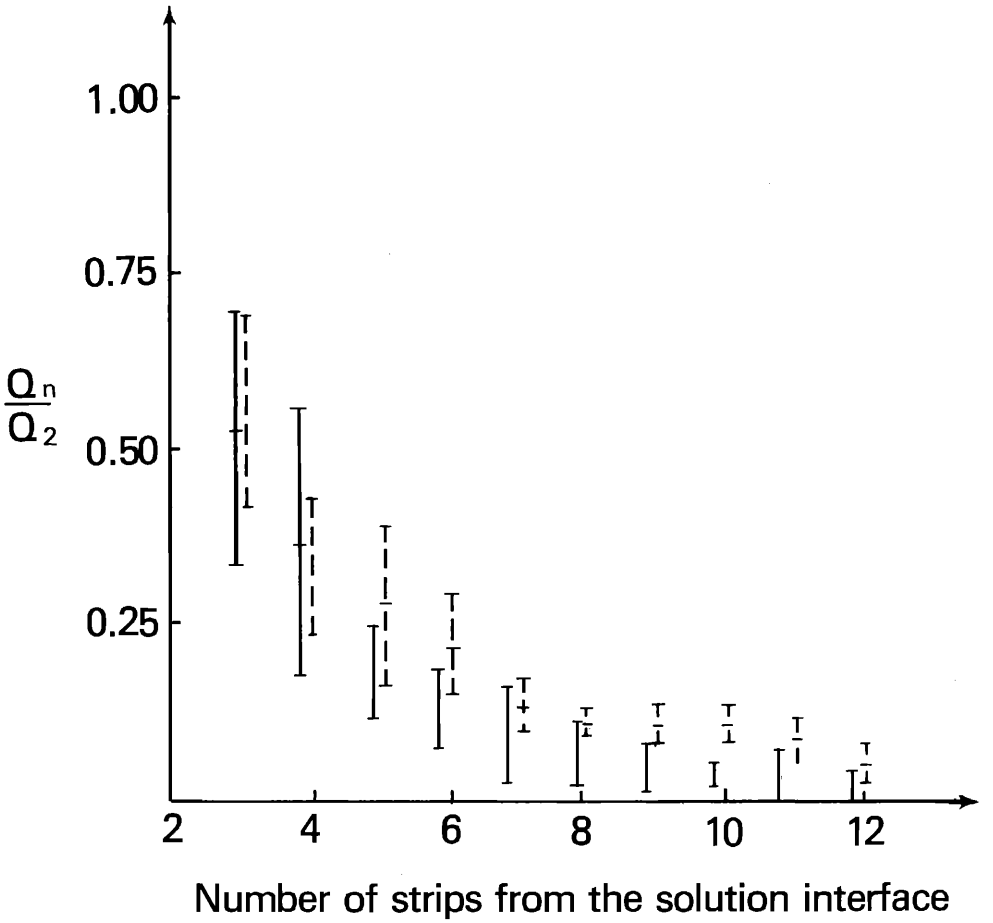

Figure 12. The distribution of sodium dodecyl sulfate (SDS) and of monocapryl glyceride (MCG) in stratum corneum in normalised units. Q_n and Q_2 denote the quantities in the n-th and 2nd strip respectively. Solid lines–SDS; broken lines–MCG. (Reproduced with permission from reference 10.)

presence or absence of charges on the molecule (3). An important conclusion that emerged from these studies is that, if the physical/chemical properties of keratins are affected by the presence of surfactants in the tissues, asymmetrical distributions of the surfactant molecules induce high degrees of anisotropies in the properties affected. This aspect of the surfactant keratin interaction has important practical implications, and will be discussed further in Section VI.

V. THE EFFECTS OF DETERGENTS ON THE STRUCTURE AND THE PROPERTIES OF KERATINS

Having discussed the uptake of surfactants from a thermodynamic and kinetic point of view, the questions of the actual location of the surfactant molecules within the keratin structure and the effects on the cosmetically important attributes of the presence of these molecules on properties of hair, skin and nails have to be considered. In a series

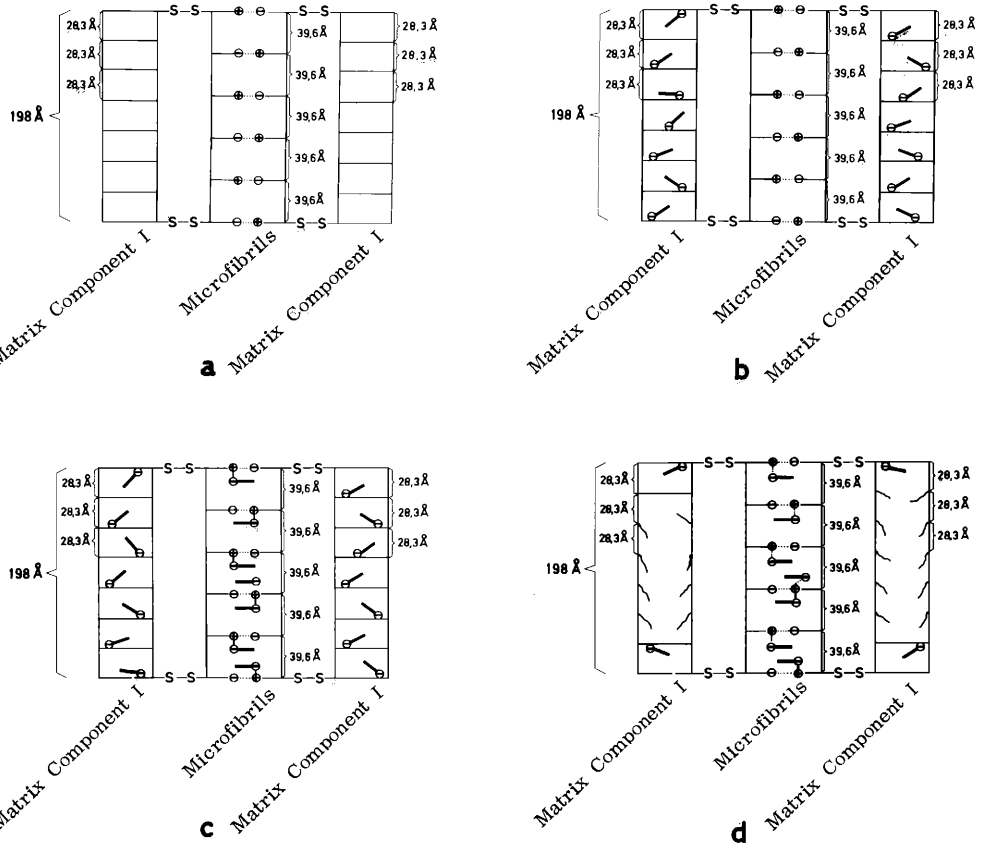

Figure 13. Schematic representation of the sequence of events that occur when surfactants penetrate keratin. For details see text. (Reproduced with permission from reference 7.)

of papers, Spei et al. investigated extensively the interaction between keratins and surfactants using low angle x-ray diffraction (11–13). From Spei's work the following sequence of events appears to take place when keratin is exposed to detergents. The first surfactant molecules which enter the keratin structure penetrate its noncrystalline regions, i.e., the matrix, and by doing so, they disturb its long-range order. This is demonstrated by the changes of the spacing at 28.3 Å that is characteristic for the structural repeat units of the matrix (Figures 13a and b). When the detergent concentration of the solution in contact with the keratin is further increased, the additional surfactant molecules gradually find their way into the more organized and crystalline microfibrillar regions of the keratin structure (Figures 13c and d). Again, this second stage of penetration is evidenced by the changes of the characteristic spacings at 39.6 Å reflections. In addition to Spei's X-ray data, results of other experimental techniques also indicate that surfactant molecules do penetrate the crystalline regions of the keratin structure. The absorption isotherms of surfactants, both on stratum corneum and on wool fibers, reveal maxima near the critical micelle concentrations (Figures 14 and 15). Since, according to thermodynamics, in a three-component system a downturn of the absorption isotherms is only possible if structural changes occur in the absorbant substrate, the results shown in Figures 14 and 15 also support Spei's

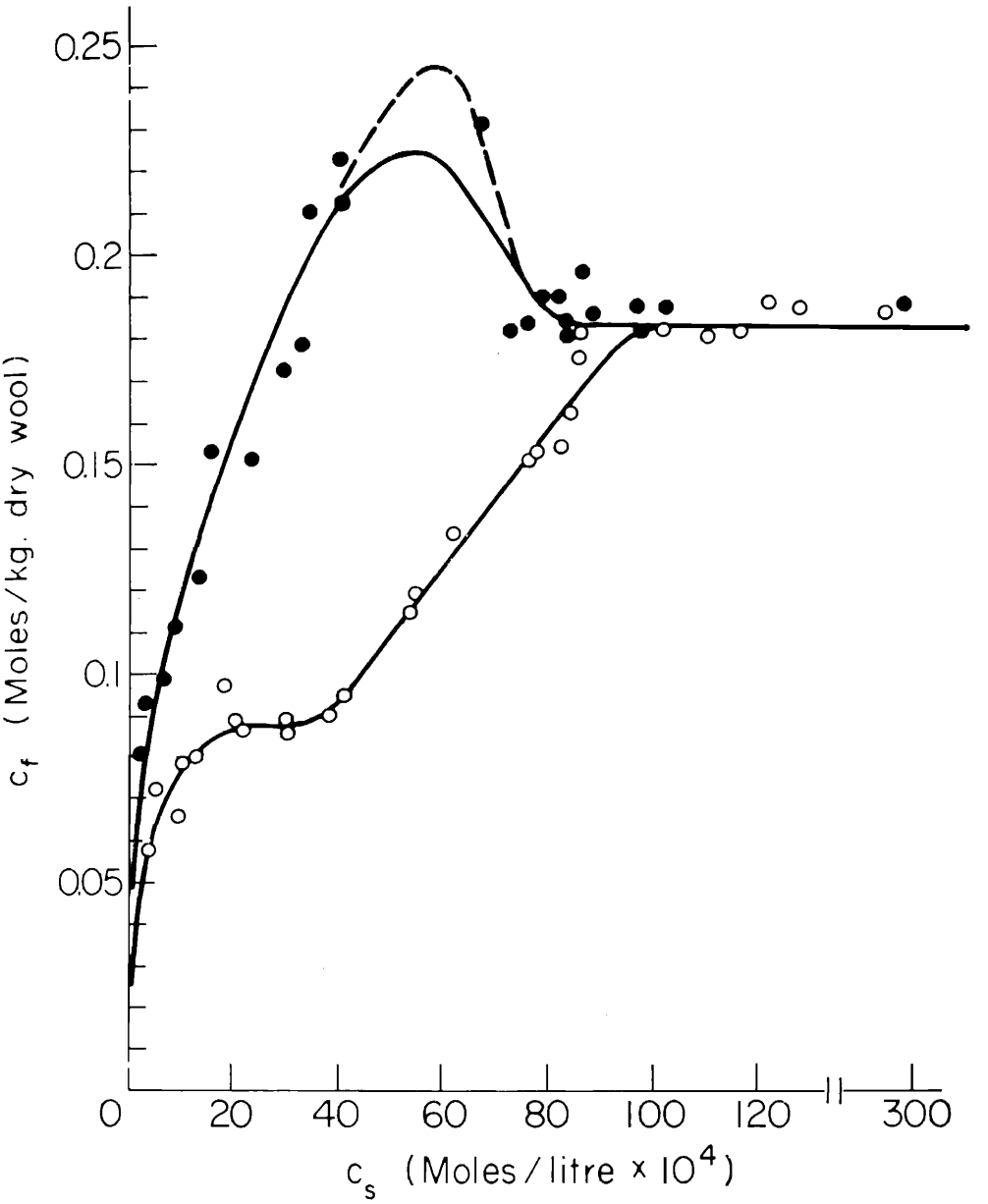

Figure 14. Isotherms for the adsorption of SDS by wool at 40°C (•) and 60°C. (0) c_f and c_s are the concentrations of SDS in the wool and in the solution, respectively. (Reproduced with permission from reference 21.)

interpretation, i.e., that surfactant molecules enter and disrupt the crystalline regions of the keratin structure. Furthermore, the drop in the uptake curve, both for wool and for stratum corneum, coincides with the concentrations where Spei has observed the penetration of the first detergent molecules into the crystalline structures. It is also interesting that, when the isotherms are measured at higher temperatures, the maxima disappear and the curves show a gradual increase towards a plateau (Figure 14). The

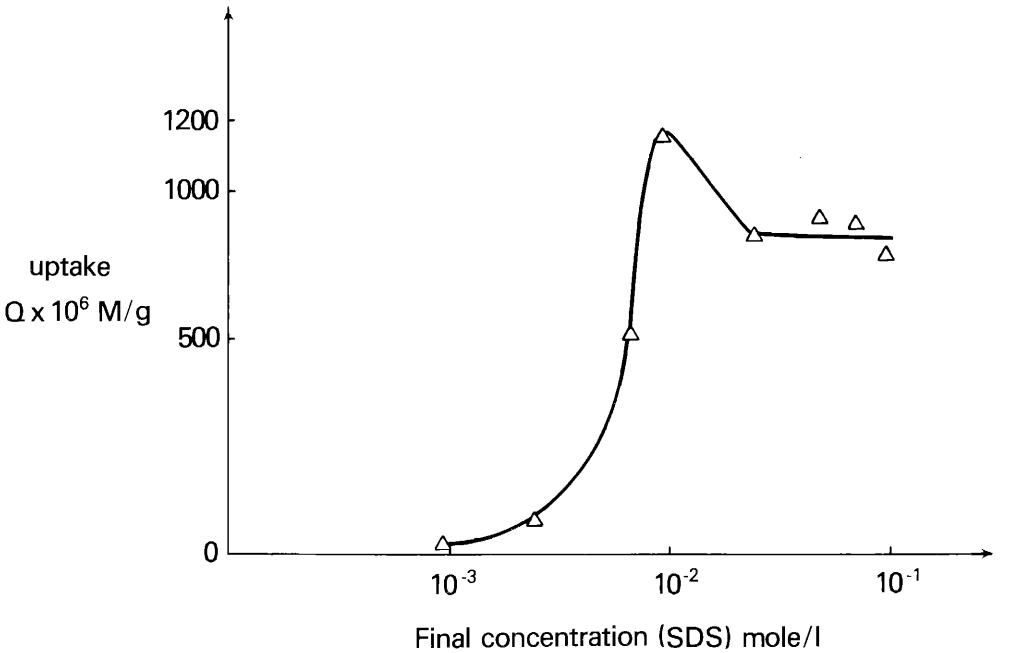

Figure 15. Adsorption isotherm of sodium dodecyl sulfate in isolated stratum corneum. (Data reproduction reference 10.)

disappearance of the maximum at higher temperature can be most probably attributed to a melting of the crystalline regions susceptible to detergent absorption.

It is only fair to point out that alternative interpretations of the various experimental data from that outlined in the previous paragraph is also possible. In particular, it has been suggested that the effects observed by Spei can also be explained by assuming that the detergents penetrate the matrix and not the microfibrils of the hair. (I am grateful to one of the referees for pointing out this fact.) Furthermore, it is also important to keep in mind that Spei obtained most of his X-ray data on mohair, which is a low sulfur-containing keratin and, hence, contains only relatively few cross-links. Owing to the higher cross-link density and the thicker cuticule, the penetration of detergents into human hair is a slower process. The effects observed by Spei on mohair can only be perceived in human hair after prolonged reduction of the disulfide bonds (12). Nevertheless, it is the author's view that the processes outlined by Spei most probably play an important role in the interaction of surfactants with human hair, especially since most hair fibers on heads are considerably weathered and, therefore, much more susceptible to surfactant penetration than the virgin human hair fibers which were used in Spei's experiments.

The effects of the detergents on the mechanical properties of keratin fibers have been investigated by Zahn et al.[14] who found that the presence of detergent in wool and hair fibers brought about a diminution of 25% Stretch Index (i.e., the work required to stretch the fibers by 25% of their original length) (Figure 16), and that the higher the detergent uptake, the larger was the drop in the value of the 25% Stretch Index, i.e., the less stiff the fibers became. Similar findings were obtained in stratum corneum by Putterman et al. (15). Zahn's results also confirmed that a proportionality existed

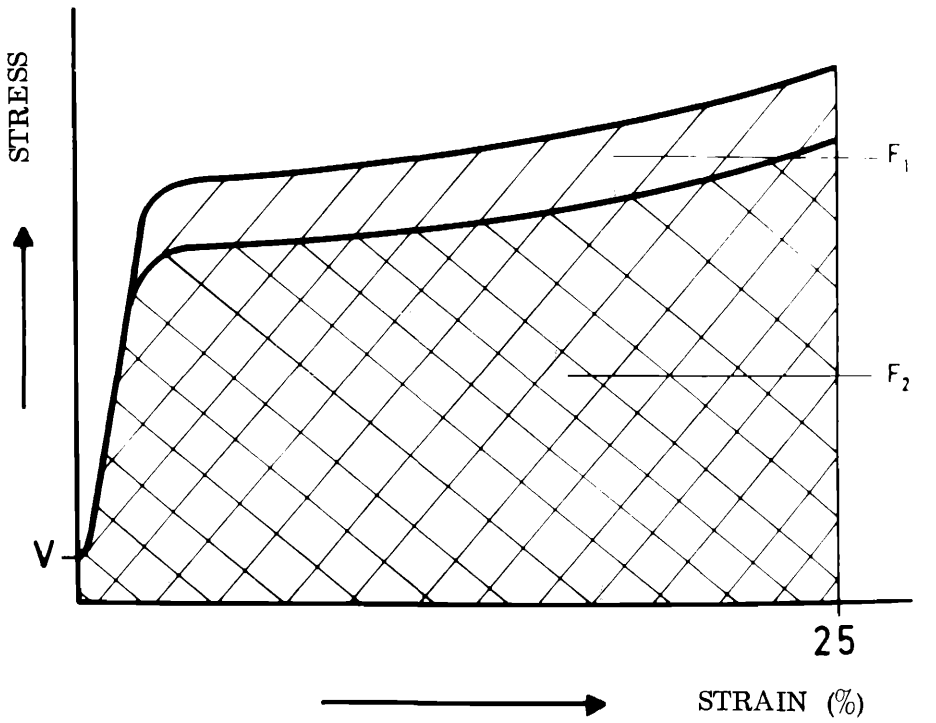

Figure 16. Typical strain-stress curve of keratin. The areas under the curves represent the 25% Stretch Indices, i.e., the work required to stretch the fiber to 25% strain. Abscissa: strain; coordinate: stress. (Reproduced with permission from reference 14.)

between the amount of detergent taken up and the reduction in the stretching work of the fibers. Furthermore, the experimental results also revealed that hexyl sulfate was more efficient than dodecyl sulfate in reducing the stretching work of wool fibers suggesting that the former compound, owing to its smaller size, penetrated the crystalline regions of the fiber with greater ease than the latter and, thus, exercised a stronger effect on the tensile properties of the wool fibers (Figure 17). It was also observed that considerable time was required before equilibrium values of the 25% Stretch Index were achieved (Figure 18). In some cases, treatment times of a few hundred hours were required for the 25% Stretch Index to reach a steady value. The above results further confirmed the conclusions reached by the X-ray diffraction and thermodynamic absorption measurements, i.e., that detergent molecules penetrate the crystalline regions of keratin and, by doing so, strongly affect the tensile moduli of these materials. The long time effects are characteristic of processes that involve conformational changes of polymer, i.e., crystalline-amorphous transitions.

VI. THE COSMETIC IMPLICATIONS OF UNEVEN DISTRIBUTION OF SURFACTANTS IN KERATIN

The two observations, (a) that surfactant molecules penetrate into the crystalline regions of the keratin fibers (e.g., hair) and sheets (e.g., stratum corneum and nails) strongly affecting their mechanical properties and (b) that the distributions of the

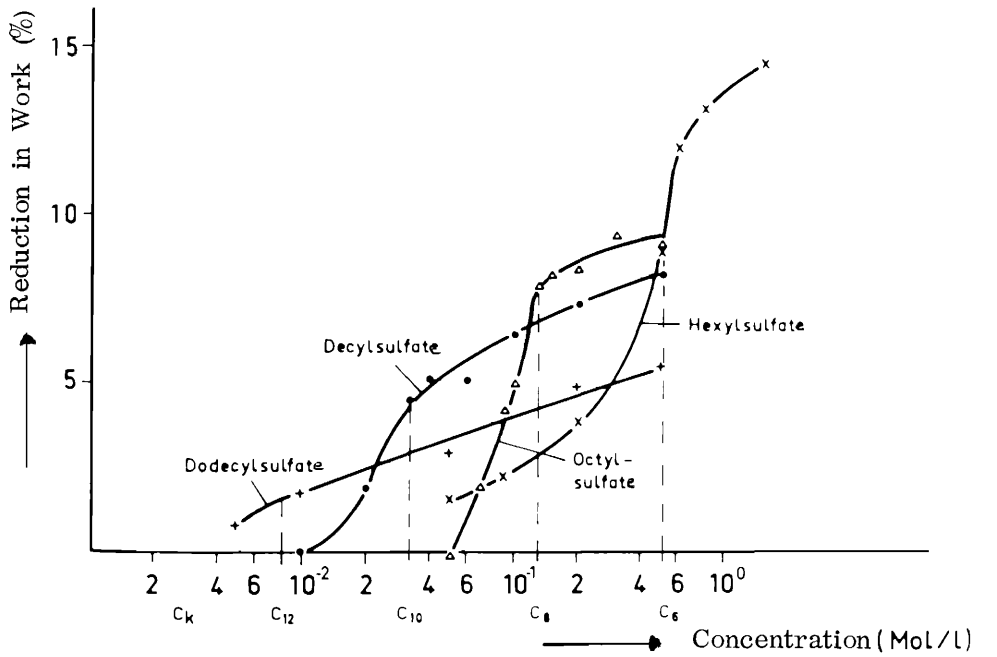

Figure 17. Percentage reduction of the value of the 25% Stretch Index of keratin fibers exposed to various concentrations of surfactants (Reproduced with permission from reference 14.)

surfactant in these tissues are highly asymmetrical, have important consequences as far as the cosmetic attributes of these tissues are concerned. To illustrate this point, let us consider for instance the case of a layered structure (e.g., stratum corneum) where each layer contains a different amount of surfactant (Figure 19). Depending on the detergent content, the elastic modulus of each layer will be affected to a different

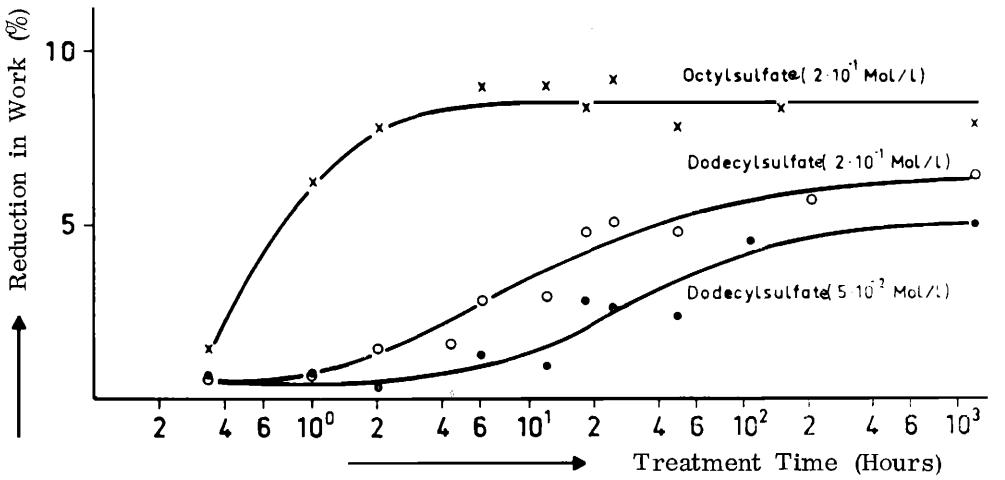

Figure 18. Percentage reduction of the 25% Stretch Index of keratin fibers as a function of time when immersed into solutions of surfactants. Abscissa: sufactant concentration. Coordinate percentage loss of wool. (Reproduced with permission from reference 14.)

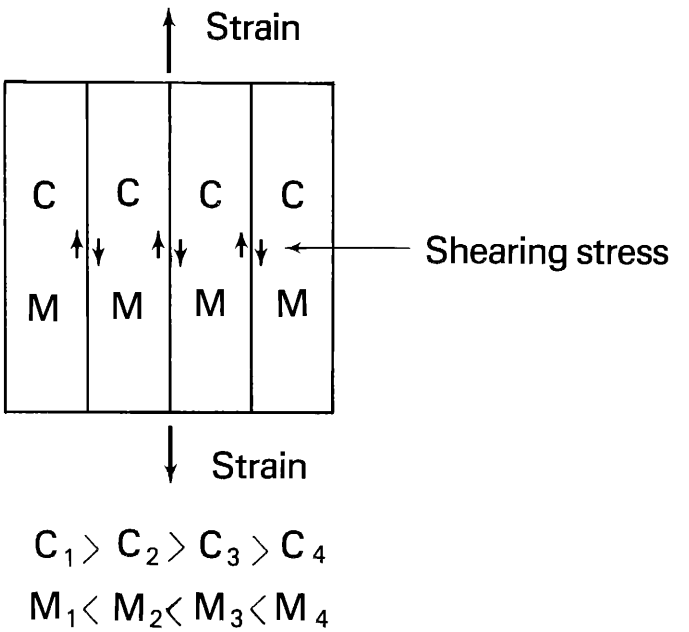

Figure 19. Schematic representation of events in stratum corneum containing an uneven distribution of detergents in the various cell layers. c_i and M_i represent the detergent concentrations and the moduli of the i-th layer, respectively.

degree: the layer nearest to the surface and containing most detergent will have the lowest elastic modulus, whereas each subsequent layer containing less and less detergent molecules will have an increasingly higher elastic modulus. If a structure of this sort is now exposed to a uniform longitudinal stress, the differences of moduli which exist between the layers will induce considerably different strains in each layer, with the net result that large shearing stresses will arise at the layer boundaries (Figure 19). Skin chapping and nail breakage as consequences of detergent exposure probably originate from this kind of physicochemical effect. It is also highly probable that materials facilitating the diffusion of materials in skin (e.g., urea, water) will bring about a more uniform distribution of the surfactants in skin and, therefore, will ameliorate the effects of detergent-induced shearing stresses.

VII. THE EFFECT OF DETERGENTS ON THE CHEMICAL REACTIVITY OF KERATINS

A variety of chemical reactions can affect keratin structure. Among these, surfactants can influence especially three important processes: the degradation of the main polypeptide chains, the reduction of the disulfide bonds and the lanthionine and lysoalanine formation from disulfide bridges. As is the case with proteins in general, keratin polypeptide chains can be broken by acid hydrolysis. Depending on the pH and the nature of the charges they carry, ionic surfactant molecules, absorbed in the keratin structure, will influence these processes by either attracting or repulsing hydrogen or hydroxyl ions. The effective concentrations of these attacking species near the peptide or disulfide bonds will be, therefore, augmented or depleted. These

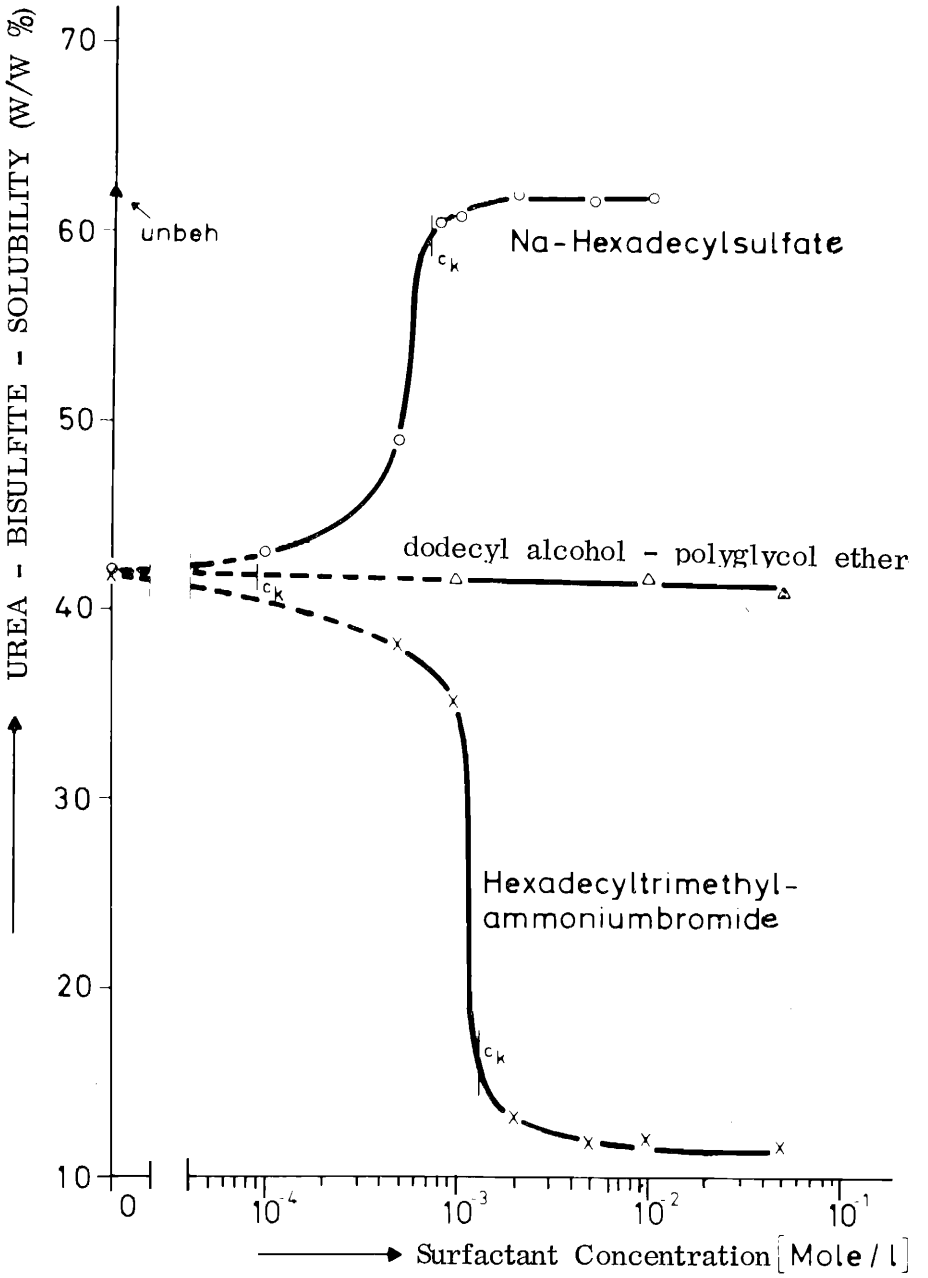

Figure 20. The urea-bisulfite solubility of wool, exposed to pH 9 solution at 60°C for 2 hr as a function of surfactant concentrations in solution. Abscissa: surfactant concentration; coordinate: urea bisulfite solubility. (Reproduced with permission from reference 18.)

processes have been studied extensively during the last few years (16). For instance, Meichelbeck and Knittel (17) determined the urea bisulfite solubility of wool samples after they had been exposed to surfactant solutions of increasing concentrations at various pH values. Under alkaline conditions, where the attacking species were the

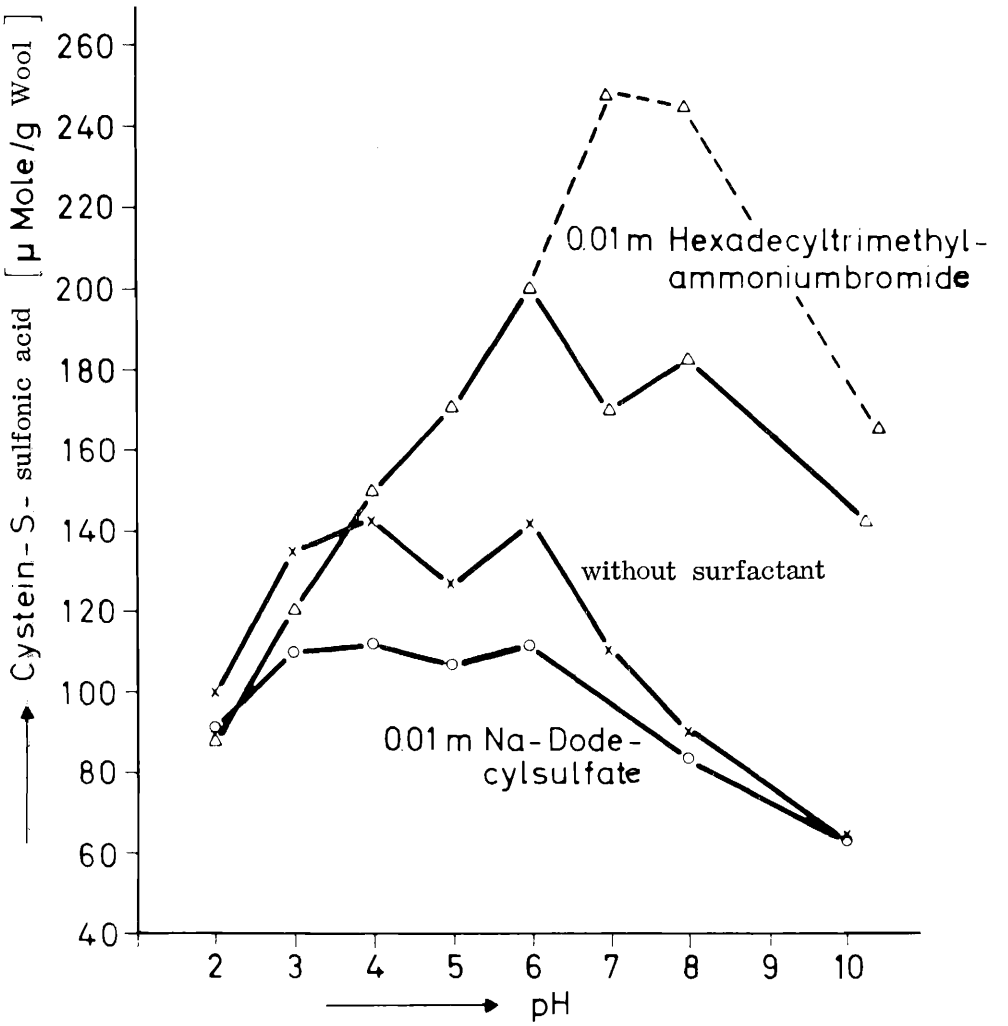

Figure 21. Cystein S-Sulfonic acid production in wool in the presence of surfactants. Treatment conditions: exposure to 0.2*M* Na_2S0_3 at 50°C for 1 hr. Abcissa: pH; coordinate Cystein-S-Sulfonic acid content. (Reproduced with permission from reference 17.)

hydroxyl ions, these authors found that the presence of anionic detergents protected the wool against chemical changes. The cationic detergents, under the same conditions, on the other hand, enhanced the damage to the fibers. Nonionic surfactants did not show any additional effect beyond the normal degradation of keratin which occurred when it was exposed to prolonged treatments of alkaline media (Figure 20). These results could be explained by assuming that the absorbed negatively charged surfactant molecules repulse the OH^- ions and, similarly, that the presence of the positive detergents attracted these attacking species to the vicinity of the disulfide bonds. Exactly the opposite type of results were obtained when the effect of cationic and anionic surfactants were investigated under acid conditions. In those cases, the attacking species were the hydrogen ions and, consequently, the cationic detergents exerted the protecting effect on the keratin.

Finally, the exclusive use of the first order of detergency on the very important reductions which

occur with the disulfide bonds of keratin when exposed to various reducing nucleophilic agents. Since the attacking species in most of these cases are negatively charged ions (e.g., bisulfite or thioglycollate ion), the presence of negatively charged detergents in the structure diminishes the rate of reactions with these attacking ions. On the other hand, cationic detergent absorbed into the keratin structures will, in fact, enhance the reactivity of the disulfide bonds with respect to nucleophilic agents and thus speed up the breaking of these important crosslinks. Again, Meichelbeck and Knittel confirmed these reactions by their experimental measurements (Figure 21).

VIII. THE EFFECT OF FORMULATION INGREDIENTS ON THE UPTAKE OF SURFACTANTS BY KERATINOUS SUBSTANCES

From the foregoing sections it is evident that during cosmetic treatments involving the use of surfactant-containing products, certain amounts of the surfactant molecules

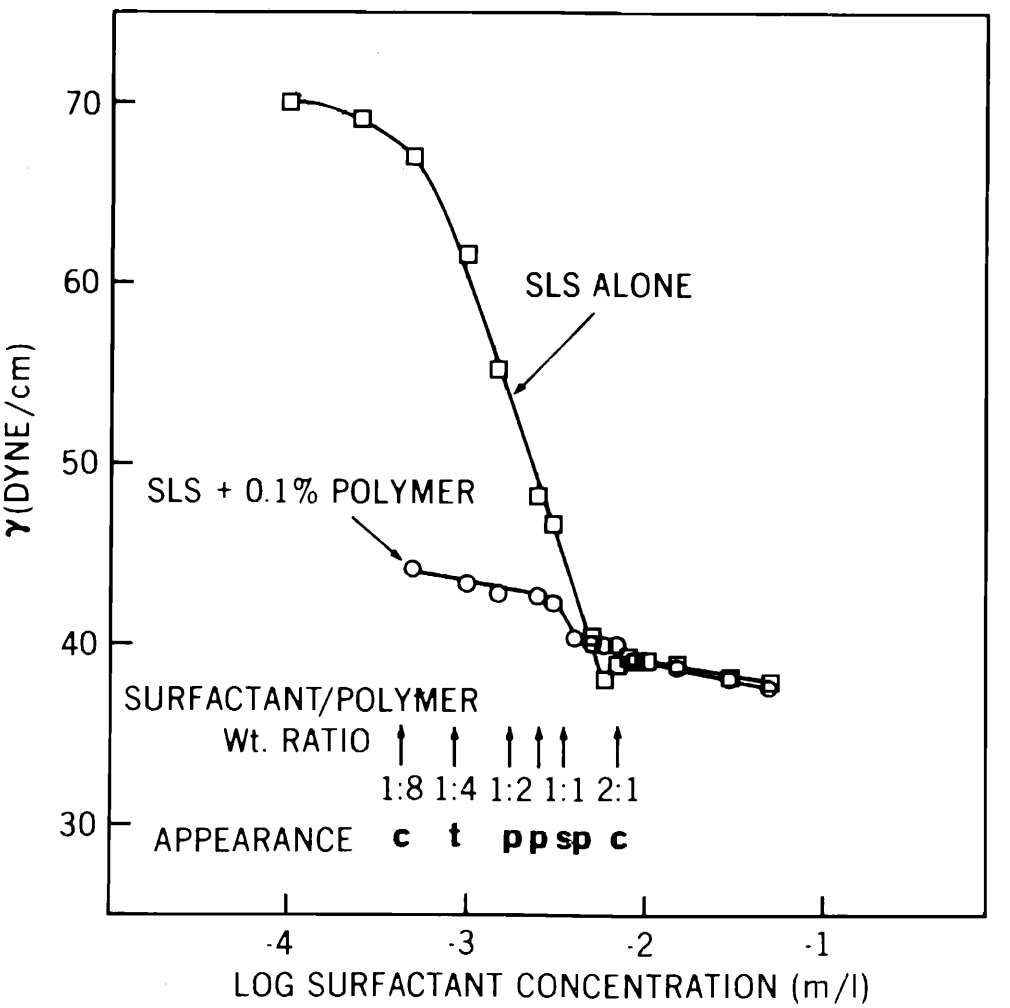

Figure 22. Surface tension, concentration curves of Na Lauryl sulfate in water at 25°C, with and without 0.1% Polymer JR. (Reproduced with permission from reference 19.)

penetrate the keratinous tissues (skin, hair and nails) affecting the properties of these tissues sometimes in a beneficial way, sometimes in a detrimental way. It is also known that many of the surfactants penetrate beyond the stratum corneum and interact with the vital tissues of the skin causing, on occasion, irritation and even sensitization. The art of product formulation is therefore to find a surfactant composition capable of achieving maximal functional effects (e.g., cleaning power) with minimal penetration of detergents into the human tissues. On the whole, the penetration of the surfactants can be regarded as being proportional to the number of monomeric (nonmicellar) surfactant molecules in the system. The functional effects of detergents will, on the other hand, generally depend in a more complicated way on the surfactant activity. As an example, let's consider a product that contains a polymer capable of complexing with surfactants (e.g., Polymer J.R.). The cleaning ability of the surfactant system (e.g., of the shampoo) will depend on its surface activity. Goddard et al. (19) demonstrated that the presence of Polymer J.R. in a surfactant solution will enhance surface activity (Figure 22). On the other hand, other experimental data also indicate that the presence of Polymer J.R. reduces the irritation potential of surfactants (20), presumably owning to complexation of the attacking free surfactant molecules. These results show, in a very vivid fashion, that given suitable formulation technology a high degree of functional efficacy can be achieved at the same time as the irritation potential of a surfactant can be diminished.

To quote another example for the importance of formulation technology in achieving the desired product attributes, let us consider Poret's (10) results with mixtures of sodium lauryl sulfate and capryl monoglyceride. Poret measured the surface tensions and the depositions into stratum corneum from solutions containing these surface active materials as functions of the ratios of the constituents and their concentrations.

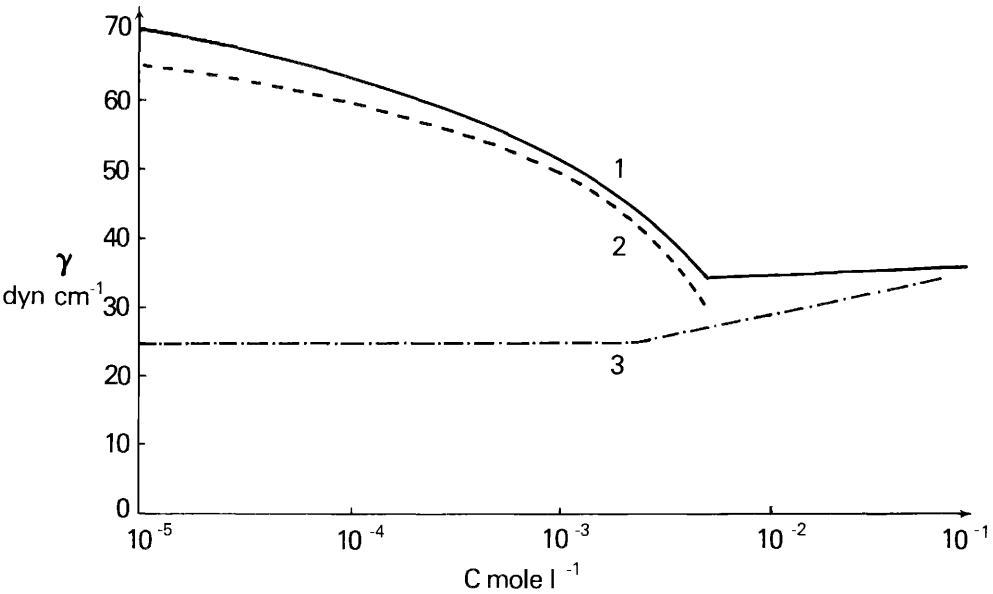

Figure 23. The surface tension of surfactant solutions as a function of concentrations. Curve No. 1—pure SDS; Curve No. 2—pure MCG; Curve No. 3—mixture of SDS with various proportions of MCG. (Reproduced with permission from reference 10.)

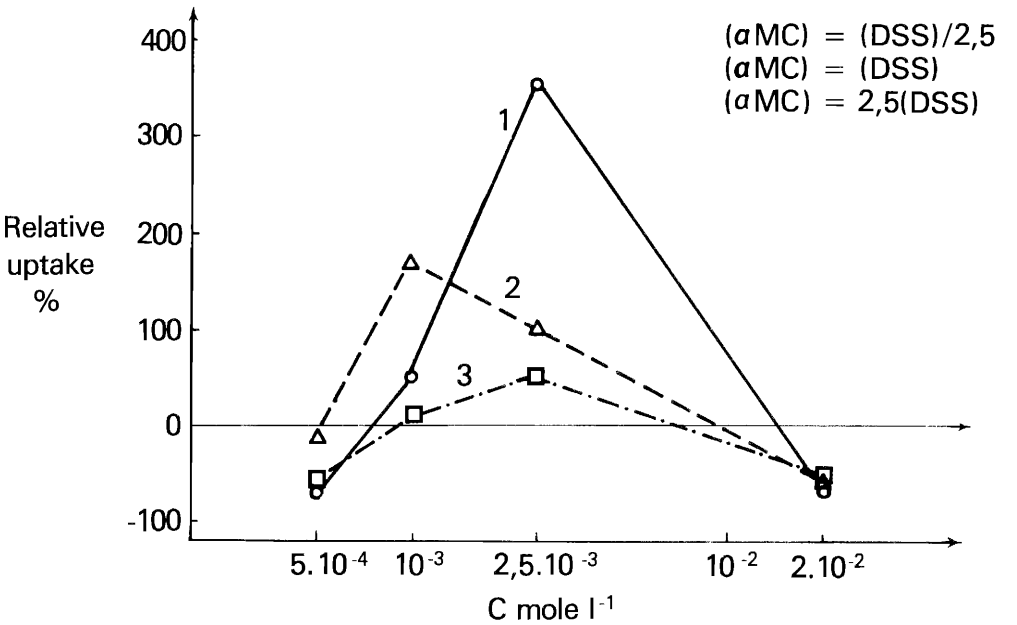

Figure 24. The relative uptake of SDS on stratum corneum as a function of concentration from its mixtures with MCG. (Reproduced with permission from reference 10.)

Whereas the surface tension was essentially independent of the ratios, and always lower than either of the solutions containing the pure constituents (Figure 23), the deposition of the monocaprylate was found to be highly dependent on the overall concentrations (Figure 24). To date no satisfactory theories have been formulated to explain these phenomena.

CONCLUSIONS

A review of the published literature reveals that surfactants penetrate into keratinous tissues, affecting their structure and physical and chemical behavior. Some of the changes that are brought about have important consequences as far as the cosmetic attributes of hair, skin and nails are concerned.

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