J. Soc. Cosmet. Chem., 29, 323–337 (May 1978)

Interaction of keratinous substrates with sodium lauryl sulfate: I. sorption

J. A. FAUCHER and E. D. GODDARD *Union Carbide Corporation, Tarrytown, NY 10591.*

Received September 9, 1977. Presented at Annual Seminar Meeting, Society of Cosmetic Chemists, May 1977, Montreal, Canada.

Synopsis

Use was made of radiotagged SODIUM LAURYL SULFATE (SLS) to determine its sorption by skin and hair. In the initial stages uptake is linear in square root of time, indicative of a diffusion process. The uptakes determined by radiotagged SLS were successfully correlated with data from a simple gravimetric method and showed that the latter procedure can be used satisfactorily under certain conditions when radiotagged compounds are not available. The influence of some additives on the SORPTION of SLS was studied. Salt increases the sorption, while nonionic SURFACTANTS (which are not themselves sorbed) substantially depress it. Finally, the relation of the sorbed SLS to water of hydration of KERATIN is examined. It is concluded that most, if not all, the sorbed material is bound to keratin, rather than existing in an "internal" solution.

INTRODUCTION

Surfactants and soaps are known to be irritating to the skin and under extreme conditions can have adverse effects on hair. Scientific study of the action of these materials is hampered by a lack of data on their uptake by various keratin substrates. The availability of sodium lauryl sulfate (SLS) in radiotagged form makes it relatively easy to study the kinetics of sorption of this model surfactant over a wide range of concentrations and times, and to explore the various effects of additives.

There are few data in the literature concerning the sorption of surfactants by human hair. Two studies (1,2) have dealt with long-chain quaternary ammonium halides (typical cationic surfactants), but both were conducted at concentrations well under 1%. A brief radiotracer study was made of sodium acyl sarcosinates (3) in which the concentration was as high as 5%. However, nothing has appeared dealing with nonionics, amphoterics or more common anionics such as sodium lauryl sulfate and its ethoxylates; nor have concentrations in the range of 10% been investigated, corresponding to the actual strength of shampoos.

The situation is similar for the substrate skin. There is a large, medically oriented literature on the percutaneous absorption of surfactants–particularly anionics like SLS, but the uptake of surfactant by the skin is not usually considered in these works. Two not-

able exceptions are Harrold and Pethica (4) and Blank and Gould (5). However, both of these papers describe only long times (18 to 24 hr) and low concentrations. Another related study deserves to be cited, namely the work of Garrett (6) on the sorption of surfactants by hide powder. Only low concentrations were employed, but the fundamental $\sqrt{t}$ dependence was shown at short times.

It is believed that the present study is the first to examine short times and high surfactant concentrations, corresponding in some degree to normal-use conditions.

EXPERIMENTAL

Undamaged and bleached hair samples were obtained from DeMeo Bros., New York City, and were used as received.

The stratum corneum from neonatal rats was used as a model for human skin. The details of preparation of these membranes have been given in a previous publication (7). This stratum corneum has well developed barrier properties, at least in respect to the transmission of water vapor, as has been shown by Singer and coworkers (8) and confirmed by our own determinations (7).

Sodium lauryl sulfate was obtained as a pure white crystalline powder from BDH Chemicals, Ltd., Poole, England. Tagged material was purchased from Amersham/Searle Corp., Arlington Hts., Illinois, in the form of small, individual ampoules. Each ampoule contained 2.47 mg of SLS with an activity of 110 microcuries. The "tag" is present as the S-35 isotope and is thus in the anion of the surfactant:

Standapol ES-2 (Henkel Co.)—sodium lauryl ether sulfate with 2 mol of ethylene oxide.

Standapol ES-3 (Henkel Co.)—sodium lauryl ether sulfate with 3 mol of ethylene oxide.

Standapol 130E (Henkel Co.)—sodium lauryl ether sulfate with 12 mol of ethylene oxide.

Tergitol 15-S-9 (Union Carbide Corp.)—the 9 mol ethoxylate of secondary C_{13} to C_{15} alcohol.

Solutions of desired concentration were made up of the nonradioactive powder and one ampoule of tagged material was added with stirring. Hair samples of about 100 mg each were placed in 20 ml of the solution for times which varied from a few minutes to 8 hr. They were then removed and rinsed twice for a few seconds to remove entrained solution. For stratum corneum the sample size was approximately 2 mg and the solution was 10 ml. In either case the exposed substrate was dissolved with Unisol (Isolab Inc.) and Unisol-Complement was added. The resulting clear solution was counted by the scintillation method on a Packard 3255 Tri-Carb Spectrometer to determine the amount of SLS sorbed. Triplicate experiments were run and averaged for each experimental point on the figures.

A GRAVIMETRIC PROCEDURE

The availability of accurate sorption data from the radiotracer experiments with SLS described below furnished a benchmark from which a simpler gravimetric technique

has been worked out for materials not available in tracer form. In studies of hair care products such as proteins, polymers and conditioners it is often of interest to determine the amount of material which is sorbed by the hair. The high cost of human hair and its difficulty in handling dictate that laboratory samples be of small size, that is of the order of 100 to 200 mg in weight. If the sorbed quantity is in the range 1 to 10% (often the case), then the incremental weight is 1 to 20 mg, an amount that is easily detected with an analytical balance. For best results the hair should always be weighed directly, not in a container. A suitable configuration is achieved by winding the 100 mg strand around one's finger and stuffing it into a 1 oz vial. Enough distilled water is added to wet the hair and the vial is left open overnight in a 50°C oven. By the next day, after drying, a well shaped curl has formed which retains its configuration and can easily be removed by forceps and placed on the balance pan.

Hair is very hygroscopic, a fact which creates a problem in gravimetric work. Thoroughly dried hair will gain several percent of its weight in moisture when it is exposed to the atmosphere for only a few minutes. It is thus extremely important to make sure that the sample being weighed is always at the same reference state relative to water vapor. For example, this could be a "bone dry" condition such as is achieved by drying over P_2O_5 or at high temperatures. However, drying by desiccants is time-consuming, while high-temperature drying tends to alter the hair protein irreversibly. On the other hand, simple equilibration for some time at ambient atmosphere is quite unsatisfactory, owing to changes of relative humidity. As a compromise, oven drying at 50°C was adopted. This is low enough so that no damage seems to occur to the hair. The amount of time required to reach equilibrium water content is of the order of 8 to 12 hr. Thus samples can conveniently be left overnight in the oven before weighing. (A 10 min period in a desiccator to cool the sample is advisable between the oven and balance.) The reproducibility achieved in this way has generally been very satisfactory. For example, two samples of bleached hair were conditioned in a 50°C oven for a day. Their weights were recorded as 104.8 and 123.4 mg. The samples were then placed in distilled water for three days, removed and dried in the oven overnight. The following day their weights were, respectively, 105.0 and 123.6 mg.

For accuracy, the hair samples should be dried and weighed several times, both initially and after sorption, until constant values are obtained. In actual practice it was usually found that the weight after the first drying does not change appreciably upon further drying. It is always advisable to run several "controls" for each sorption experiment; these are hair samples which are exposed to distilled water for the same time as the duration of the sorption. Normally the controls will return to their initial weight; but in some cases systematic (*i.e.,* more than one sample) deviations of 0.5 to 1 mg can occur. This is possibly related to large changes of ambient laboratory humidity. Such deviations should be taken into account for the sorption samples.

Some discussion about rinsing procedure is in order here. To a certain extent the method followed must be adapted to the material which is sorbed. Thus, for a cationic polymer, which is very tenaciously sorbed, the hair should be thoroughly rinsed several times. The polymer sorbed will not come off easily even with vigorous washings; and more important, the viscous polymer solution which is easily entrapped in the hair must be removed or erratic results will be recorded. At the other end of the spectrum are substances like salts (see below for results on NaBr). In this case sorption is very weak and thorough rinsing completely removes the salt; a different procedure must be

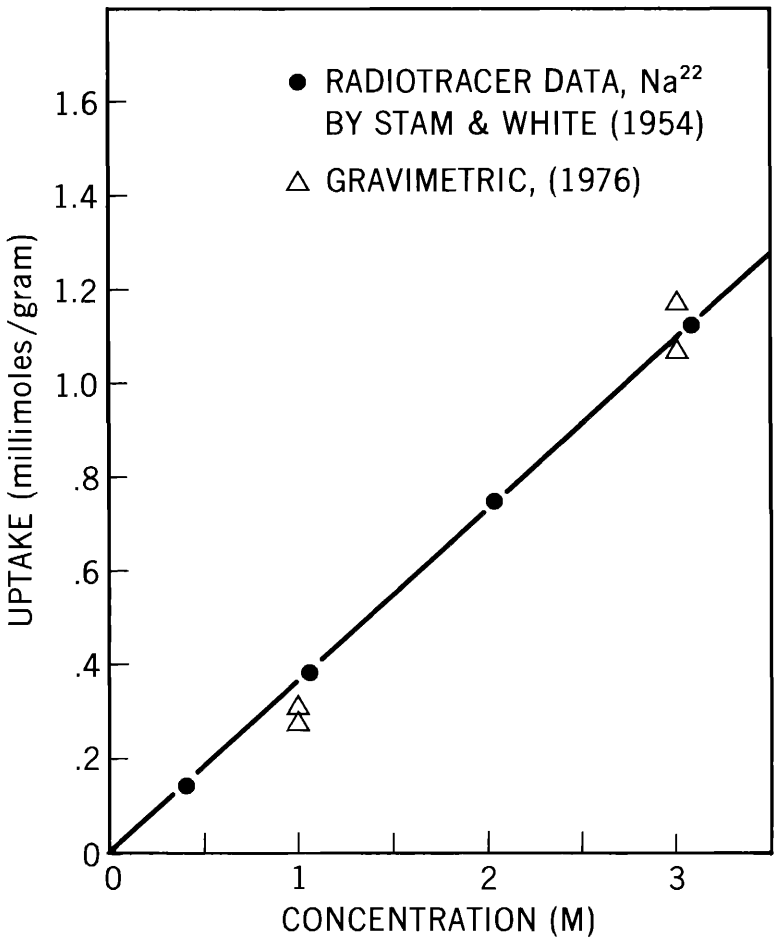

Figure 1. Sorption of sodium bromide by blonde hair

followed, which consists in simply patting dry the hair fibers with tissue. This effectively removes entrapped liquid. The weight of a tress treated in this way is surprisingly reproducible and corresponds to a kind of "fully hydrated" state. The anionic surfactant sodium lauryl sulfate (also treated below) corresponds to an intermediate case. The surfactant is fairly tightly bound by the hair substrate and is located internally as well as on the surface. However, upon very thorough washing (15 to 30 min) a third or more of it will be desorbed. Hence a compromise protocol is advisable, such as two or three successive short rinses in distilled water to remove adhering liquid and foam.

With suitable care the gravimetric procedure outlined above has yielded results which are quite close to those obtained by radiotracers, as shown in the following cases:

Sodium bromide, NaBr. Stam and White (9) have reported on the uptake of NaBr by undamaged blonde hair from aqueous solution, using a Na^{22} tag. Their results for several concentrations are given in Figure 1 and show a linear relation between sorption and concentration. Our gravimetric data (also with undamaged blonde hair) done in duplicate at two concentrations are plotted in the same figure. The agreement is surprisingly good, considering that the hair samples are completely different. Note that

this is a relatively favorable case owing to the large weight of sodium bromide; 1 millimole/g corresponds to about 10% by weight.

Sodium lauryl sulfate (SLS). In this instance, the uptake of SLS from 10% solution was measured on a single series (three samples for each time period). The solution was tagged with the compound described in the experimental section. First, weighing was done according to the gravimetric method above, yielding the open triangles of Figure 2. The samples were then dissolved and counted for radioactivity content following the procedure of the experimental section. This gave the solid circles of Figure 2. The agreement of the two methods is excellent indeed.

Thus, for relatively favorable cases (bleached hair as substrate and large uptakes), sorption of some materials by hair can be determined gravimetrically with reasonable accuracy. (The authors have not found it practical to adapt a similar procedure to stratum corneum as substrate.)

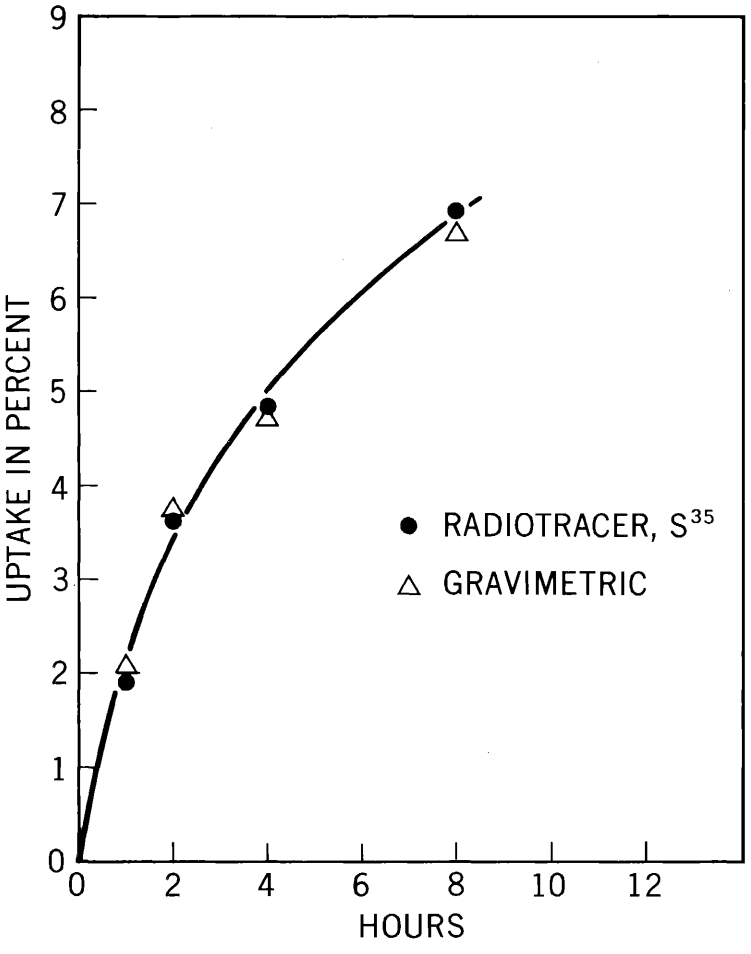

Figure 2. Sorption of 10% sodium lauryl sulfate by bleached hair; gravimetric and radiotracer determinations were made on the same samples of hair

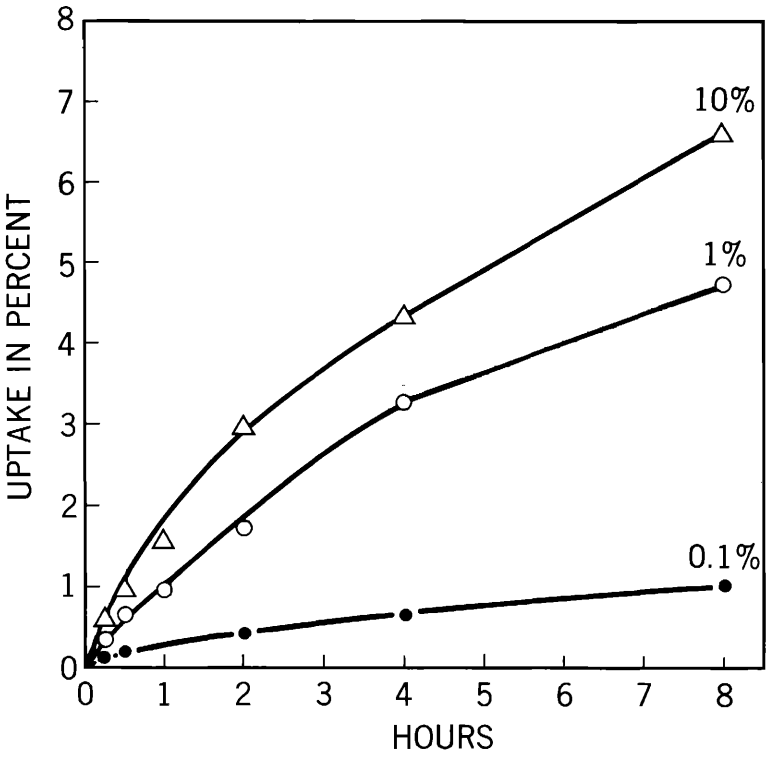

Figure 3. Sorption of sodium lauryl sulfate by bleached hair

RESULTS AND DISCUSSION

SODIUM LAURYL SULFATE

Typical sorption curves at various concentrations are shown in Figure 3 for bleached hair and in Figure 4 for stratum corneum. Similar curves were obtained for undamaged hair and the uptakes in that case were approximately an order of magnitude less than found for bleached hair. For all these substrates the course of sorption follows closely a linear dependence on the square root of time, consistent with a diffusion process. In Figure 5 the data are plotted in this manner for both bleached and undamaged hair. A linear dependence is observed except for the first 15 to 30 min, where a sort of "lag time" is observed. Analogous behavior has been noted before in the dyeing of wool, a physically similar type of process (10,11). The initial lag is characteristic of the presence of a surface barrier, which in this case is postulated to be the so-called epicuticle (12). The data for stratum corneum (Figure 6) also shows good linearity in $\sqrt{t}$ but there is no evidence of a surface barrier.

The slopes of the uptake – $\sqrt{t}$ lines can be regarded as a measure of the rate of sorption and it is evident that these rates continually increase with concentration. Thus Figure 7 shows the uptakes at 1 hr (which are proportional to the slopes) plotted against the total surfactant concentration for stratum corneum and bleached hair. An interesting feature occurs in both cases: the rate function closely approximates two straight lines which intersect at the critical micelle concentration, CMC, *i.e.*, the point

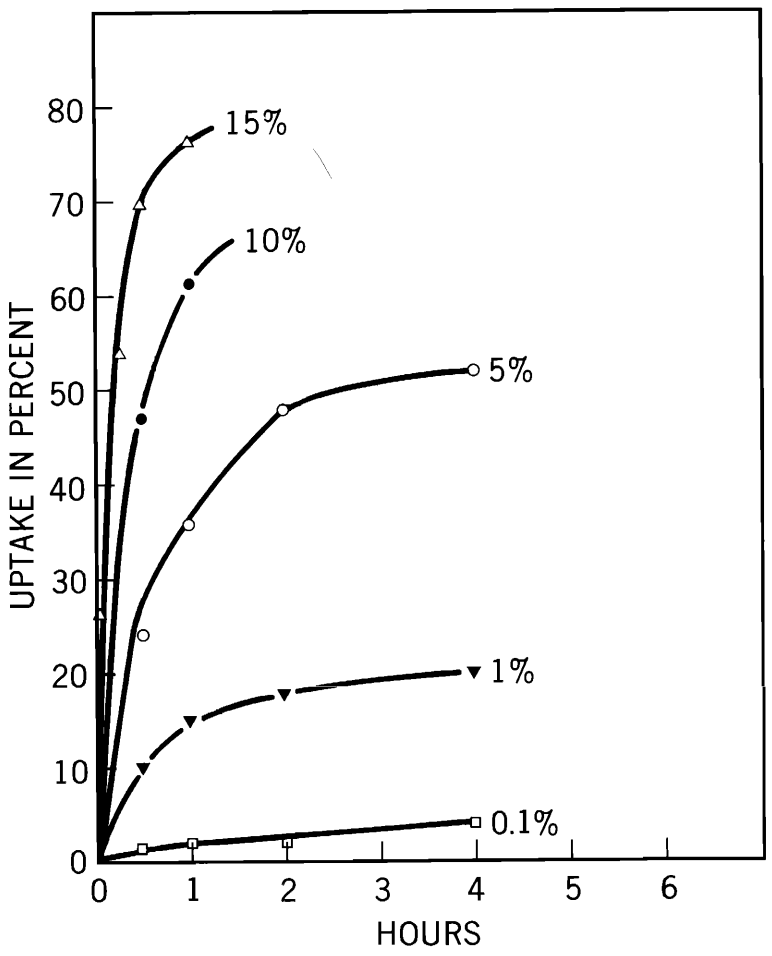

Figure 4. Sorption of sodium lauryl sulfate by stratum corneum

where micelles begin to form. (For SLS this concentration is 0.24%.) Undamaged hair also shows this phenomenon, but the rates are considerably lower than for bleached hair.

It is not surprising that the CMC is important in terms of sorption rate. The diffusion mechanism of sorption strongly suggests that it is the monomer species which enters the substrate. Above the CMC most of the added surfactant is known to exist in the solution as micelles, *i.e.,* roughly spherical aggregates of 50 to 100 surfactant molecules. These entities do not seem to penetrate the keratin, probably because of the combination of size and negative charge. Little is known about the precise monomer concentration above the CMC, although it is often stated that it remains constant. There is evidence, however, that it may increase slowly. For example, osmotic pressure data (13) show a pattern of two intersecting lines similar to Figure 7, but the measurements were not extended very far above the CMC. Mysels (14) in some ingenious dialysis experiments has shown that the rate of passage of SLS through a membrane impermeable to micelles continues to increase above the CMC and he cites this as evidence for increas-

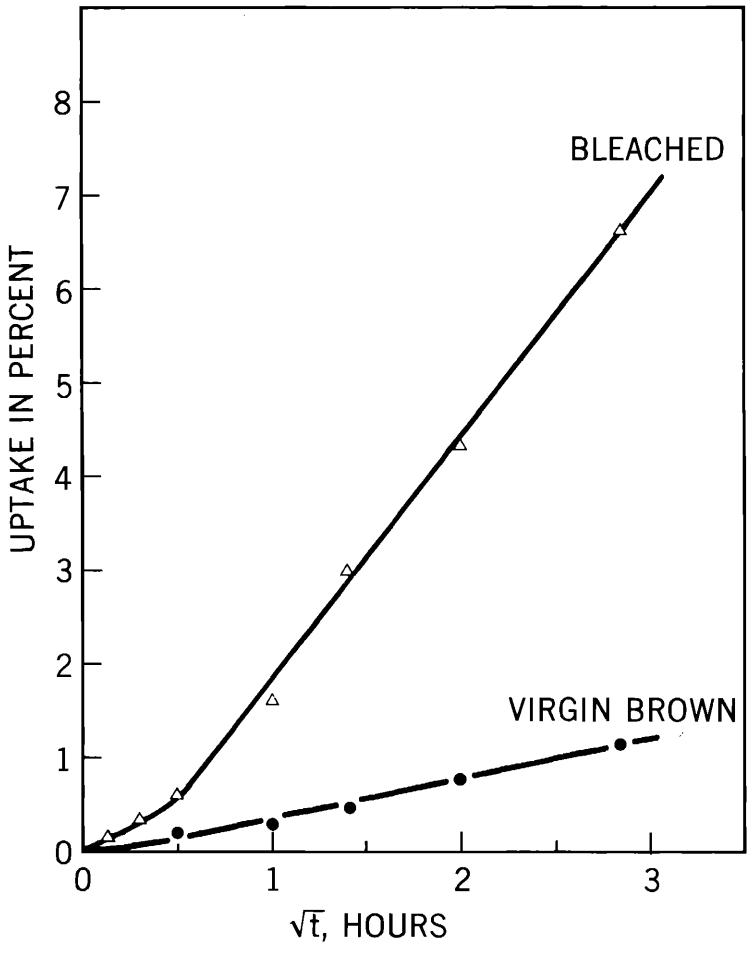

Figure 5. Sorption of 10% sodium lauryl sulfate by bleached and virgin brown hair

ing activity of the monomer in this region. Unfortunately it is very difficult to make direct measurements that are unambiguously related to the SLS monomer concentration in the region well above the CMC. Thus, while it is not clear that monomer concentration in fact does increase there, the sorption data shown here are consistent with such an interpretation and they show the same kind of phenomenon found in the dialysis experiments of Mysels.

THE DIFFUSION PROCESS

From the uptake *vs.* $\sqrt{t}$ curves a rough estimate can be made of the diffusion constant of SLS in the keratinous medium, either hair or skin. For hair, the formulation commonly employed is that which represents diffusion into an infinitely long cylinder at short times (9):

$$\frac{Q(t)}{Q(\infty)} = \frac{4}{r}\sqrt{\frac{Dt}{\pi}}$$

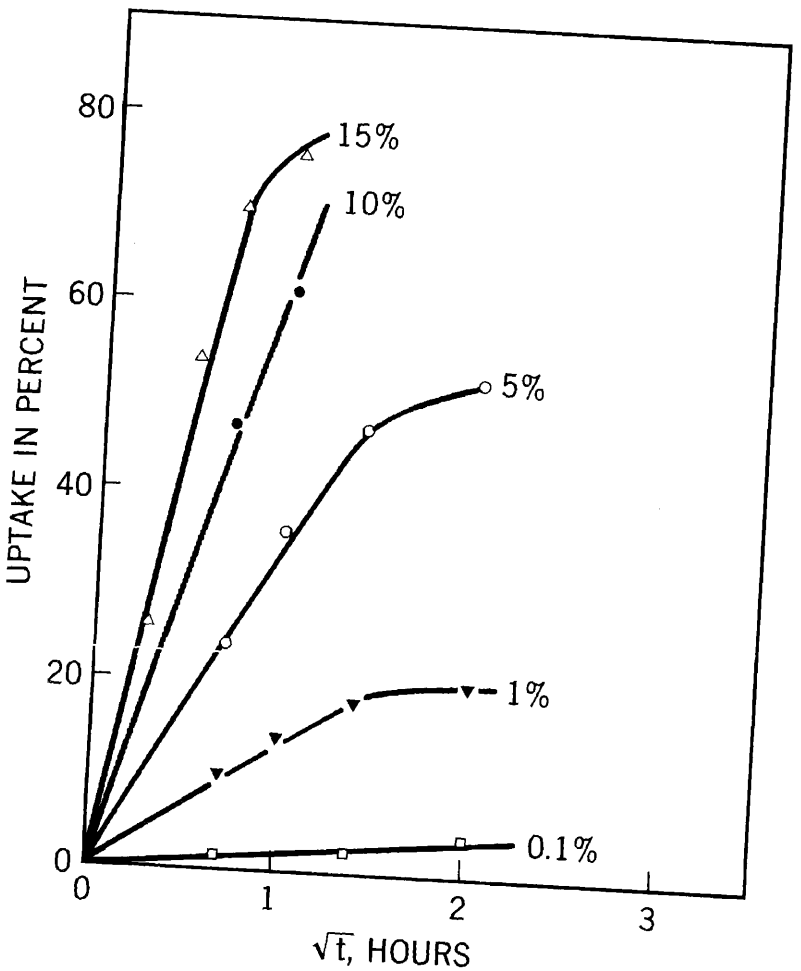

Figure 6. Data of Figure 4 *vs.* $\sqrt{t}$

where r is the radius of the hair fiber, D is the diffusion constant and Q (∞) is the "equilibrium" uptake, *i.e.*, at very long times. If r is taken as 25×10^{-4} cm and a rough estimate is made for Q (∞) by measuring uptake after several days, one obtains for bleached hair D = 1 to 3×10^{-11} cm²/sec and for undamaged hair D = 1 to 2×10^{-12} cm²/sec. Within the uncertainty of estimation of values for Q (∞) the magnitudes of the diffusion constant D were found to vary only slightly for the concentration range between 0.1 and 10%. They compare well with values reported by Griffith (15), 1×10^{-11} cm²/sec, and by Chen (16), 4×10^{-11} cm²/sec, in both cases for wool, a closely related substrate. These authors made use of the formula cited above.

In the case of skin, we prefer to use the well known formula of A. V. Hill (see reference 7 for a derivation):

$$Q(t) = 2C_0\sqrt{\frac{Dt}{\pi}}$$

where Q is the uptake in g/cm², C_0 is the external concentration in g/cm³, t is the

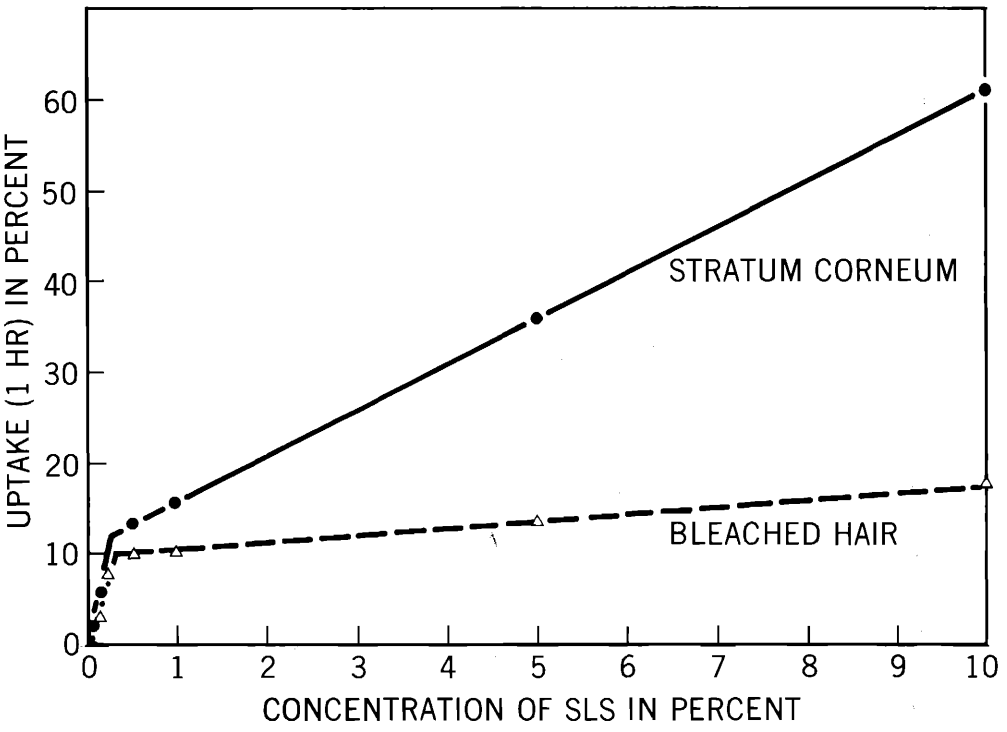

Figure 7. Concentration dependence of sorption rate: uptake of sodium lauryl sulfate by stratum corneum and bleached hair

time in seconds and D is the diffusion constant. The diffusing species is assumed to be the SLS monomer; hence C_0 corresponds to the total solution concentration only in the range below the CMC (0.24%). Using data at 0.1 and 0.2% one obtains by this formula $D = 3$ to 7×10^{-9} cm^2/sec, about three orders of magnitude higher than in undamaged hair but still considerably lower than for SLS in water.

SORPTION OF SODIUM LAURYL ETHER SULFATES

Having measured the sorption of 10% SLS by a simple weighing procedure, it was of interest for comparison to determine the uptakes of closely related surfactants: Standapol ES-2, ES-3 and 130-E. These are, respectively, the 2, 3 and 12 mol ethoxylates of SLS and they represent a chemical series which increases in ethylene oxide content. Radiotagged samples of these materials are not available, so the gravimetric procedure described above was used. In Figure 8 their uptakes *vs.* time are plotted and compared to SLS. Bleached hair was the substrate. There is clearly a reduction in sorption with increasing number of ether groups in the surfactant molecule—a reduction which also persists on a molar plot. There are several possible explanations for this effect. The simplest is that the molecules increase in size in this series and hence have more difficulty getting into the hair structure. Also very convincing is the fact that the CMC decreases markedly for these compounds as the ethylene oxide content increases (17). Thus the monomer concentration available for diffusion will be a decreasing func-

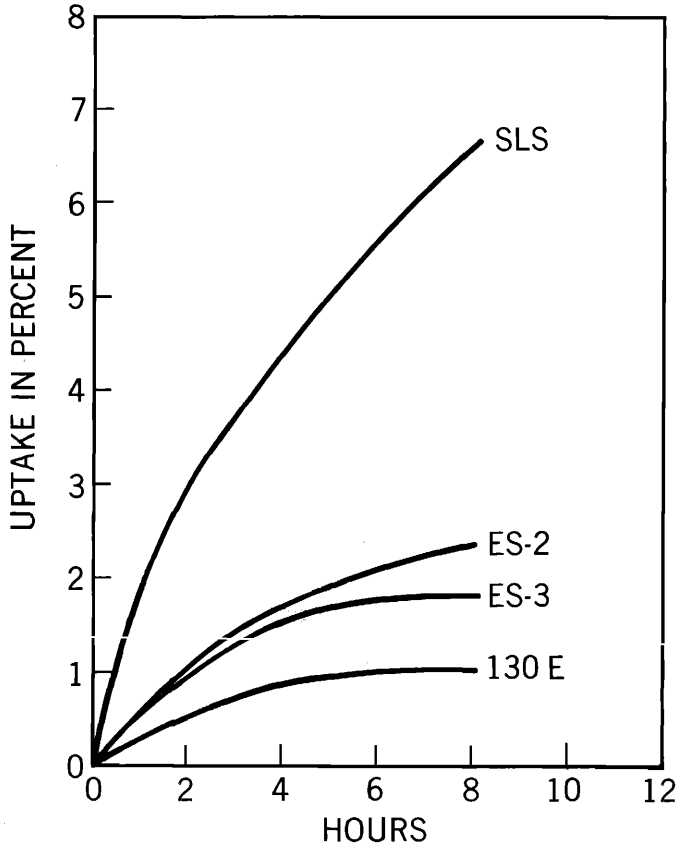

Figure 8. Sorption of sodium lauryl ether sulfates by bleached hair from 10% solution

tion also. This decreased sorption correlates well with the well known milder properties of highly ethoxylated anionic surfactants compared to SLS.

THE EFFECT OF ADDITIVES

A feature of SLS sorption is that it is strongly influenced by the addition of certain other compounds. For example, sodium chloride generally causes an increase in sorption. This effect is well known from work on wool (15,16). It is even more pronounced with stratum corneum as the substrate, as the data in Figure 9 show. Harrold and Pethica (4) found the same phenomenon with finely divided epidermal keratin. Salt decreases the CMC of SLS, so the monomer concentration will be lowered in its presence. It seems, therefore, that the salt must act on the substrate in a way that makes it more available to the surfactant or by a nonspecific electrical screening effect.

On the other hand, the addition of a nonionic surfactant such as Tergitol 15-S-9 considerably decreases the sorption of SLS, both for hair and skin. This is not due to competition between the two surfactants for sites in the keratin, because the nonionic material is hardly sorbed at all by itself. Instead it is known that mixed micelles of the two surfactants are formed. For a very similar system Schick and Manning (18) have

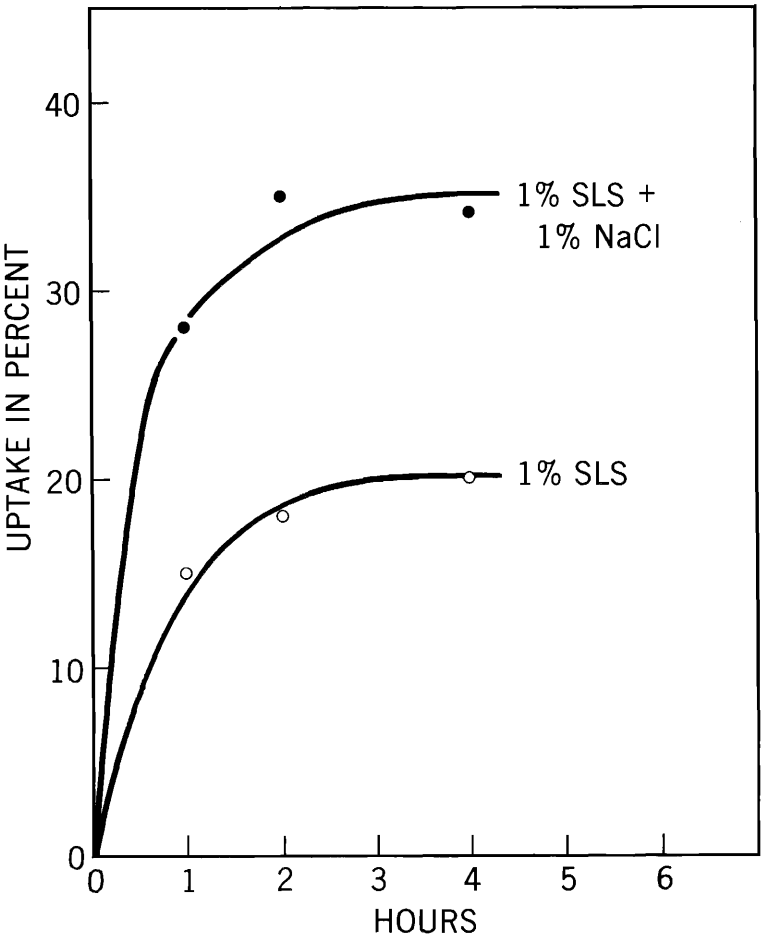

Figure 9. Effect of salt on the sorption of sodium lauryl sulfate

shown that even small additions of a nonionic surfactant have a large effect in lowering the CMC of sodium lauryl sulfate. This brings about a lowering of the SLS monomer concentration and, hence, lower sorption. Figure 10 demonstrates the effect in a striking way. This furnishes a physico-chemical explanation of the findings of Finkstein (19) who showed that a reduction of irritation of anionic shampoos occurs on the addition of nonionic surfactants in spite of the fact that the total surfactant concentration increased. In this case, lower irritation is attributed to decreased sorption of the anionic surfactant by proteins of the skin and cornea.

RELATION OF SORBED SURFACTANT TO WATER OF HYDRATION

Both hair and stratum corneum absorb water when placed in solution. It is therefore conceivable that some, if not all, of the sorbed surfactant may be present as a solute in this "internal" solution, rather than being truly bound to the keratin. The analytical method employed here does not distinguish these cases. It is not easy to decide this point conclusively, but the available evidence indicates that the surfactant is bound to the substrate.

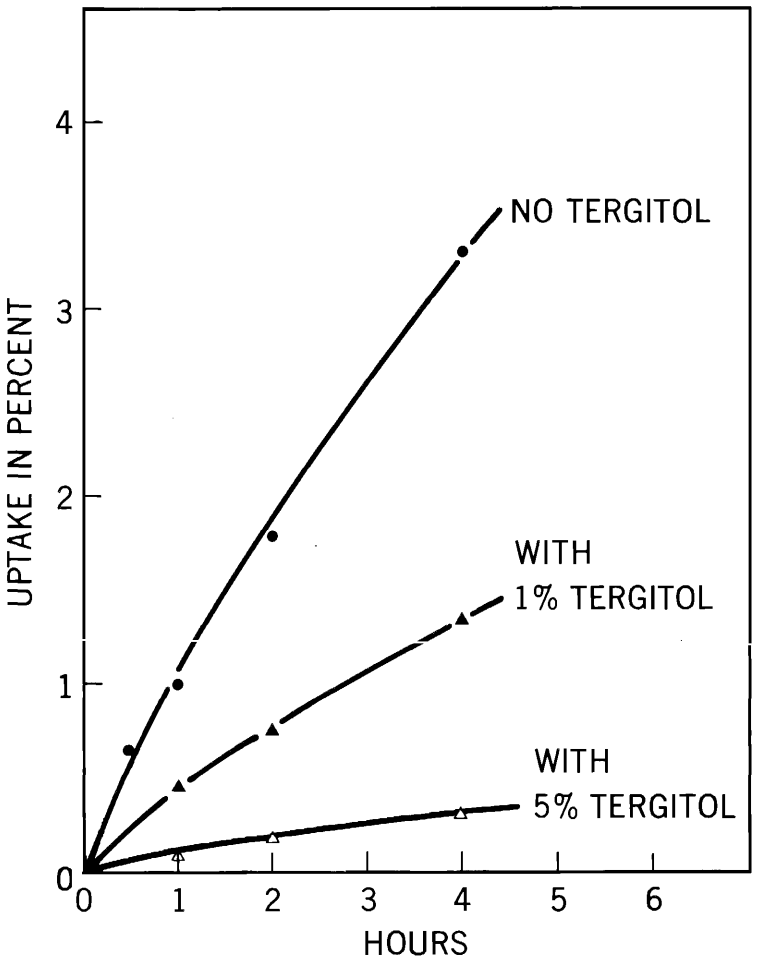

Figure 10. Effect of a nonionic surfactant on the sorption of sodium lauryl sulfate by bleached hair

For undamaged hair the water of hydration amounts to about 35% by weight of the dry substrate; this water is absorbed in less than 1 min. However, the SLS sorption, as shown in Figure 1, goes on for many hours. Furthermore, at low solution concentration of SLS the ultimate amount of surfactant taken up by hair can amount to ten times as much as would be calculated solely from the "external" solution. A study has been made by NMR of the mobility of water in hydrated hair (20). In this work it was found that such water is quite immobile and tightly bound to the keratin. It seems unlikely that SLS can exist as a normal solute in such an environment.

The case of stratum corneum is somewhat different in that this substrate absorbs as much as 1000% of its own dry weight over a period of many hours when immersed in aqueous solution. A detailed study of this water (21) shows, however, that much of it is quite restricted in mobility and probably located in the interior of the keratin cells. Again, it seems unlikely that this water of hydration can behave like the bulk "external" solution; in particular, the existence of ordinary micelles therein is improbable because of exclusion effects. Figure 11 shows two curves which compare the actual measured

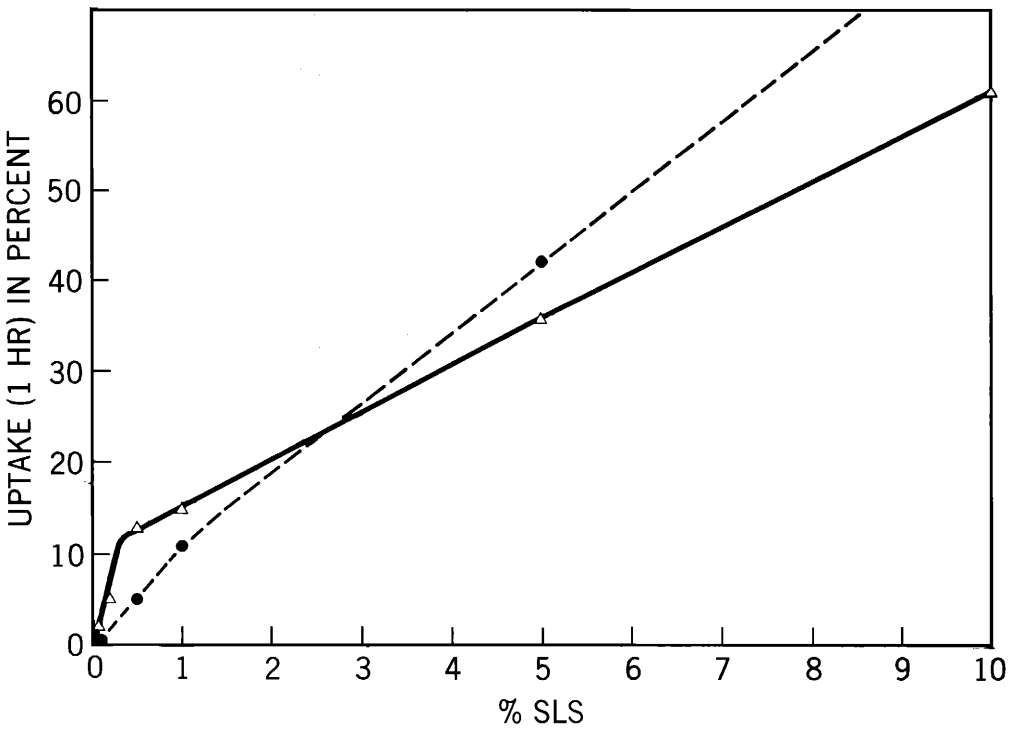

Figure 11. One hour uptakes of sodium lauryl sulfate in stratum corneum: solid line, as measured experimentally; dotted line, calculated by assuming that water of hydration has the same composition as the external solution

uptakes of SLS at 1 hr with the calculated uptakes at each concentration assuming that the water of hydration or "internal" solution has the same concentration as the "external" solution. The latter curve was calculated from swelling data obtained at a 1 hr exposure for a number of concentrations of SLS. It will be noted that the uptakes at low concentrations (below the CMC) are much greater than the calculated uptakes. But at high concentrations (above 5%) the calculated uptakes are larger than the measured ones. This lack of agreement clearly shows that the internal solution does not have the same concentration as the external one. It does not exclude the possibility, however, of some SLS monomer existing in free solution inside the stratum corneum. The evidence above suggests that this possible state is unlikely to amount to more than a small fraction of the measured uptake. In this connection it may be recalled that collagen and protein in general can bind large amounts of SLS. Nelson (22) has shown that as much as 1.1 to 2.2 g of SLS/g of protein can be bound under the most favorable conditions. Thus the inference that all of the SLS uptake reported here is bound to the keratin is not unreasonable. More light could be shed on this point by a detailed NMR study of the state of the lauryl sulfate anion in hydrated stratum corneum and hair.

CONCLUSIONS

It has been shown that the uptake of anionic surfactants by hair and stratum corneum membranes is appreciable. With sodium lauryl sulfate, SLS, the uptake increases markedly with concentration even above the critical micelle concentration, and it also

increases in the presence of added salt but decreases in the presence of added nonionic surfactant. Lauryl ether sulfates are sorbed to a lesser extent than SLS and their uptake decreases with ethylene oxide content.

By comparison of sorption data obtained by radiometric and gravimetric techniques, it has been demonstrated that a simple weighing technique can be employed for measuring the uptake of surfactants and simple salts, in view of their relatively high sorption values.

REFERENCES

(1) G. V. Scott, C. R. Robbins and J. D. Barnhurst, Sorption of quaternary ammonium surfactants by hair, *J. Soc. Cosmet. Chem.*, **20**, 135 (1969).

(2) P. Finkelstein and K. Laden, The mechanism of conditioning of hair with alkyl quaternary ammonium compounds, *Appl. Polymer Symp.*, No. 18, 673 (1971).

(3) M. F. Nelson, Jr. and D. Stewart Jr., The adsorption of N-acyl sarcosines on various protein materials, *J. Soc. Cosmet. Chem.*, **7**, 122 (1956).

(4) S. P. Harrold and B. A. Pethica, Thermodynamics of the adsorption of small molecules by proteins, *Trans. Faraday Soc.*, **54**, 1876 (1958).

(5) I. H. Blank and E. Gould, Penetration of anionic surfactants into skin, *J. Invest. Dermatol.*, **33**, 327 (1959).

(6) H. E. Garrett, Detergents—what they are and how they work, *Trans. St. John Hosp. Dermat. Soc.*, **51**, 166 (1965).

(7) J. A. Faucher and E. D. Goddard, Sorption of a cationic polymer by stratum corneum, *J. Soc. Cosmet. Chem.*, **27**, 543 (1976).

(8) E. J. Singer, P. C. Wegmann, M. D. Lehman, M. S. Christenson and L. J. Vinson, Barrier development, ultrastructure, and sulfhydryl content of the fetal epidermis, *J. Soc. Cosmet. Chem.*, **22**, 119 (1971).

(9) P. B. Stam and H. J. White, Jr., The application of radiochemical techniques to the study of the interaction of hair fibers with aqueous solutions, *Text. Res. J.*, **24**, 785 (1954).

(10) J. A. Medley and M. W. Andrews, The effect of surface barrier on uptake rates of dye into wool fibers, *Textile Res. J.*, **29**, 398 (1959).

(11) J. A. Medley and M. W. Andrews, The kinetics of wool dyeing, *Text Res. J.*, **30**, 855 (1960).

(12) N. H. Leon, Structural aspects of keratin fibers, *J. Soc. Cosmet. Chem.*, **23**, 427 (1972).

(13) W. C. Preston, Some correlating principles of detergent action, *J. Phys. Chem.*, **52**, 84 (1948).

(14) M. Abu-Hamdiyyah and K. J. Mysels, The dialysis of sodium dodecyl sulfate, *J. Phys. Chem.*, **71**, 418 (1967).

(15) J. Griffith, "The Uptake of Sodium Dodecyl Sulfate by Wool," *Proc. 3rd Internat. Congr. Surface Activ.*, Cologne, 1960, Vol. 4, pp 28–36.

(16) J. C. Chen, The Interactions of an Anionic Surfactant with Keratin Fibers, Ph.D. Thesis, Princeton University, Princeton, New Jersey, 1971.

(17) I. J. Lin, "Hydrophobic Properties of Long-Chain Ionic Surfactants," in Colloid and Interface Science, Vol II, M. Kerker, Ed., Academic Press Inc., New York, New York, 1976, pp 431–443.

(18) M. J. Schick and D. J. Manning, Micelle formation in mixtures of nonionic and anionic detergents, *J. Am. Oil Chem. Soc.*, **43**, 133 (1966).

(19) A. W. Finkstein, "Eye Irritation Studies on Some Common Shampoo Surfactants," paper presented at the Annual Scientific Meeting of the Society of Cosmetic Chemists, New York, New York, December 1976.

(20) J. Clifford and B. Sheard, Nuclear magnetic resonance investigation of the state of water in human hair, *Biopolymers*, **4**, 1057 (1966).

(21) R. L. Anderson, J. M. Cassidy, J. R. Hansen and W. Yellin, Hydration of stratum corneum, *Biopolymers*, **12**, 2789 (1973).

(22) C. A. Nelson, The binding of detergents to proteins, *J. Biol. Chem.*, **246**, 3895 (1971).