

SURFACE-ACTIVE AGENTS IN THE COSMETIC INDUSTRY*

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IN SOME RESPECTS AN excursion into the realm of surface activity is like going with Alice into Never-Never Land, where up is down and down is up. More often it is an application by sound logic of familiar physico-chemical principles.

SURFACE CHEMISTRY

The formulation of cosmetics depends largely on the chemistry of surface forces and phenomena. In most such products, one phase has to be uniformly and permanently dispersed in another. Whether the particles dealt with are of colloidal size or are much larger the principles of colloid chemistry are those which apply.

Classical colloid chemistry is the study of special properties of substances which have been dispersed to the colloidal range. Such particles are intermediate in size between those in molecular solution and those just visible in an ordinary microscope. Surface chemistry is the study of interfacial phenomena, and as such it provides a theoretical

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background for the behavior of colloidal systems, and for the behavior of many other systems which are not ordinarily considered colloidal. However in general usage, the term colloid chemistry is often used as a synonym for surface chemistry.

Suspensions of fine particles in liquids, as in liquid make-up or toothpaste, are frequently not of colloidal fineness. Nevertheless the specific interfacial area is great enough for surface effects to become important. Other types of systems with large interfacial areas are powders, emulsions, foams, and mists. Most cosmetic products either exist in one of these forms or are converted to one of them in use.

IMPORTANCE OF SURFACE CHEMISTRY IN COSMETIC SCIENCE

Considerations of surface chemistry become important when large specific surface areas are involved. In applying cosmetic products to the skin or hair, usually a small amount of product must cover a large area. This introduces considerations of wetting and adhesive forces between the cosmetic and the

skin, surface changes at the interface between cosmetic and skin and at the interface between cosmetic and air, penetration into skin crevices, and sorption by the skin.

Many cosmetic products are emulsions of one type or another. Questions of emulsion formulation and stabilization are primarily questions of surface chemistry. Other cosmetic products are mixtures of finely powdered materials or suspensions of finely powdered solids in aqueous or oily bases. In the latter class are toothpastes, lipsticks, mascara pencils, and liquid make-up. Securing properly formulated products which will not tend to soften, harden, or separate, which will have and maintain proper color, covering power, texture, etc., depends on applications of principles of surface chemistry; the specific interfaces here are those between two liquids or between a liquid and a solid.

Certain cosmetic ingredients depend for their effect on ability to form a foam or lather. Among these are lather shaving creams and bubble baths. Others are expected by the user to foam under conditions of use, and therefore adequate foaming must be secured. These include shampoos, soaps, and most dentifrices. In foam formation, the interface between water and air is the important one.

Soaps, shampoos, and dentifrices are expected to clean skin, hair, and teeth, respectively. This introduces the broad field of surface chemistry known as detergency. That subject is too extensive to be covered

here, since so many phases of surface activity are involved in detergency. Accordingly we should like to limit this discussion to the particular phases of surface chemistry dealing with emulsification and dispersion.

DISPERSION AND EMULSIFICATION

In making cosmetics, one may be dispersing a powdered solid in oils, as for lipsticks, or in water, as for toothpaste. One may be mixing and dispersing powders in each other, as in making face powders. One may disperse a liquid in a powdered solid, as when perfume oil is incorporated in face powder, or flavoring oil in tooth powder. Most commonly of all, one disperses one liquid in another to form an emulsion. Cold creams, vanishing creams, various special skin creams, cleansing creams, hand and face lotions, brushless shaving creams, permanent wave creams, and "milki-fied" shampoos are a few of the many types of cosmetic emulsions. Satisfactory appearance and stability of the product depends upon the correct performance of the dispersion step. That is why the theory is worth discussing in some detail.

ROLE OF MECHANICAL FORCE

Regardless of how stable a disperse system may be once it has been formed, mechanical work is usually necessary first, in order to obtain the dispersion. The importance of proper dispersion in cosmetic manufac-

ture is shown by the number of mixing and dispersing devices used. In addition to the various types of ordinary mixing devices, we have colloid mills, homogenizers, roller mills, microatomizers, etc. Each is best fitted for certain types of work. Rather than dwell upon the mechanical features of these devices, let us consider the physico-chemical factors which control dispersion, so that we can see what can and what cannot be accomplished by mechanical dispersing devices. Most of this discussion will be about dispersion of liquids in liquids, or emulsification:

Interfacial tension between oil and water hinders the dispersion of oil into small droplets when an attempt is made to form an emulsion by agitation. A definite shearing force is required to break a droplet into smaller droplets, and the interfacial tension resists that force. Such shearing forces are set up during agitation by differential currents of flow within the liquid. Bearing in mind the fundamental principles of viscous flow, it follows that the force pulling apart two points in a differential flow field will be proportional to the distance between those points. If those two points are conceived to be on the surface of a droplet, the force tending to tear that droplet apart will be seen to depend on the size of the droplet. Consequently with a given degree of agitation, droplets below a certain size will never experience forces strong enough to tear them, and hence a given force of agitation, no

matter how long continued, will not produce an emulsion below a certain droplet size, as long as interfacial tension is constant.

During the earlier stages, the average droplet size will be decreasing and, for that reason, the rate of dispersion will be decreasing. Also the number of droplets and hence the rate of collisions between droplets, will be increasing. Therefore the rate of coalescence, which depends on the rate of collisions, will be increasing. Eventually a state of dynamic equilibrium is reached, where rate of dispersion equals rate of coalescence. If a greater rate of agitation were used, a greater degree of dispersion would be achieved at the equilibrium state.

Now let us suppose the agitation stopped. Since the dispersing forces no longer exist, collisions caused by brownian motion, thermal currents, etc., will cause gradual coalescence until eventually we have two separate layers. Ordinarily the oil will be lighter than the water. When agitation has ceased, the oil droplets will all tend to rise toward the top of the liquid mixture. There they will be forced into contact with each other by buoyant forces, and will hence coalesce much more rapidly than if they had remained suspended throughout the liquid.

Another kinetic factor which can affect emulsification is that of energy barriers. There is a close analogy with ordinary chemical reactions. Probably no emulsion is entirely stable. That would occur only if interfacial tension were zero;

but this is the condition required for solution, and two such liquids would therefore be miscible. However, an emulsion may be stable enough for practical purposes. A chemical reaction may involve a decrease in free energy and thus be thermodynamically possible. However a molecule, before reacting, may have to acquire a large amount of energy in order to form an activated complex. This energy is surrendered when the reaction occurs and hence does not figure in the net energy of the reaction. Nevertheless if this "barrier" energy is high, the rate of reaction will be very small. Similarly two droplets, to coalesce, may have to overcome an energy barrier imposed by the droplets having similar electrical charges. The charges may not lower the free energy of coalescence substantially, and thus not alter the thermodynamic tendency toward coalescence. However, they may have a great effect on rate of coalescence by forming a high energy barrier. So an emulsion can be stabilized in the sense of greatly reducing the rate of coalescence, without affecting fundamental instability as determined by interfacial tension.

Ordinarily when a fresh interface is generated, the final equilibrium interfacial tension is reached approximately in a small fraction of a second. Further, electrical barrier forces are often not great. Consequently, interfacial tension is a rough guide to ease of emulsification and rate of breaking of the emulsion formed, but with numerous excep-

tions. All emulsions are inherently unstable, since coalescence of emulsified phase will, by reducing area of interface, reduce interfacial free energy.

ROLE OF EMULSIFYING AGENT

Emulsions of practical interest have at least three components: Two liquids—one of which is nearly always water or an aqueous solution—and an emulsifying agent. The emulsifying agent must concentrate at the oil-water interface. There it forms films which stabilize the emulsion. Like all surface-active compounds, emulsifying agents combine polar and non-polar groups in the molecule in proper balance to give the desired effect. Various mechanisms are possible:

1. The emulsifying agent, if a soluble surface-active agent, forms an oriented molecular layer at the interface, and thus reduces interfacial tension. This facilitates rupture of droplets during agitation and permits formation of a finer emulsion by agitation forces. The very fact that an emulsion is fine reduces its rate of breaking. According to Stokes' Law, small droplets will rise to the top of the liquid more slowly than large droplets. As was noted earlier, forcing together of droplets at the surface of the mixture is an important factor in causing separation.

Further, low interfacial tension decreases the rate of separation by decreasing the proportion of collisions which are effective in causing

coalescence of droplets. Thus interfacial tension will often roughly predict rate of separation. It follows that many widely used emulsifiers lower interfacial tension markedly. This is true of the classic emulsifier, soap. Soaps are the emulsifying agents in cold creams, conventional vanishing creams, and hand lotions, as well as many other cosmetic creams and lotions. An example of a product which can be formulated with a synthetic agent but not with soap is antiperspirant cream. The usual formulation is a type of vanishing cream containing aluminum salts. A water-soluble surface-active agent is required to form the cream emulsion, but soap would be precipitated completely by the aluminum ions. Many synthetic agents are not sensitive to aluminum ions and can be used.

2. The emulsifying agent may consist of microscopic or even macroscopic particles which concentrate at the interface. Such particles would have to have suitable wetting characteristics and not tend to be strongly wet by, and hence pass completely into, either the oil or the aqueous phase.

As in the previous case, the essential point is that the free energy of the disperse liquid-liquid system, normally much higher than that of the separated liquids, is reduced by the presence of emulsifying agent at the interface. Here, however, the free energies of the solid-aqueous and solid-oil interfaces must be considered.

Thus many powdered substances

can have an appreciable emulsifying value. Insoluble inorganic pigments aid in stabilizing liquid make-up preparations. Bentonite is an especially effective emulsifier of this type, owing to its colloidal particle size.

3. The emulsifying agent may create a high energy barrier and thus, without necessarily lowering the thermodynamic "tendency" of droplets to coalesce, greatly reduce the rate of breaking. The barrier may consist of a charge imparted to the droplets by ionic emulsifiers. It may consist of a continuous hydrated film which has measurable rigidity and which prevents the oil portions of two colliding droplets from actually making contact. If the film is highly hydrated, so that there is an increase in viscosity at some distance out from the droplet, considerable clumping of droplets together or flocculation may occur without actual coalescence and breaking of the emulsion. An emulsion of this type may cream rapidly but break very slowly.

Classical gums such as tragacanth, karaya, and acacia, as well as modern synthetic gums such as carboxymethylcellulose and polyacrylates, function as emulsifiers of this sort. Also, by increasing the bulk viscosity, they slow collisions between emulsified drops and decrease the rate of creaming. Thus they may be valuable auxiliaries in emulsions stabilized primarily by surface-active agents. This is particularly true in liquid emulsions such as hand lotions.

It has long been known that some emulsifiers tend to create and stabilize oil-in-water (O/W) emulsions, and others water-in-oil (W/O) emulsions. Many attempts have been made to classify emulsifiers according to this tendency. Probably the most general rule is that emulsifiers will tend to make that liquid which preferentially wets them or preferentially dissolves them, the outer phase. Thus cetyl alcohol is strongly overbalanced in the non-polar direction, and it shows a definite tendency to stabilize W/O emulsions. Glyceryl monostearate has a more effective polar group and can be made to stabilize either O/W or W/O emulsions. Because it is not far from the point of optimum balance, for this specific purpose, its effect can be influenced by relatively small proportions of decidedly unbalanced emulsifiers. Sodium stearate, which has a still more effective polar group, shows a strong tendency to form O/W emulsions. Solid emulsifiers may be classified similarly, depending on which phase preferentially wets them. Too strong preferential wetting by either phase, however, prevents concentration at the interface, and is similar to great unbalance in the structure of a molecularly-dispersed emulsifier, whereby the agent becomes ineffective.

The classic emulsifier for W/O emulsion is lanolin. This material is rich in the higher alcohols known as sterols. It is not too difficult to separate the sterol fraction and incorporate it in a mineral oil or petrolatum base. This gives the

"absorption bases" which are useful as emulsifiers without the odor and tackiness of lanolin. Lanolin and absorption bases are widely used as emulsifiers and skin emollients in cosmetic creams. It is easy to formulate creams analogous to cold creams, but with lanolin or an absorption base as the emulsifier. The currently popular emulsion hair dressings generally contain lanolin, both for its emulsifying value and its effect on the hair.

EMULSIFIER FORMED IN SITU

A freshly created interface in a three-component system may require considerable time to reach its equilibrium interfacial tension. Let us suppose that in a specific system the equilibrium tension is very low—less than one dyne—but that several minutes or hours are required to reach that value, and that a freshly formed interface has a high tension—say 15 or 20 dynes per cm. During agitation, as soon as any portion of the oil begins to be divided, fresh interface with a high interfacial tension is formed. Therefore the oil resists subdivision. However, if by vigorous action, the oil is subdivided and maintained in very small droplets for an appreciable time, those droplets will achieve the low equilibrium tension, and the emulsion will be comparatively stable.

Here is an example from the field of metal cleaners. We found that a solution of 5 per cent of an oleate soap in kerosene shows high initial tension—12-14 dynes—against water. Over a period of several

minutes, this value falls to one dyne or less. On the other hand if the soap is formed at the interface by bringing together a solution of alkali in water and a solution of fatty acid in kerosene, the interfacial tension is at once found to be less than one dyne. From this, the emulsification behavior of these systems can be correctly predicted. When the alkali in water is shaken very slightly with the fatty acid in kerosene, a highly stable, finely dispersed emulsion forms at once. However, when the soap in kerosene is shaken with water, even though agitation is prolonged and violent, most of the kerosene does not emulsify. As soon as shaking is stopped, it rises to the top as a free solvent layer. But if this mixture is passed through a mixer in which a great deal of work is put into the system, a colloid mill for example, a finely dispersed emulsion is formed, and this emulsion is as stable as the one formed by combining alkali in water with fatty acid in kerosene.

Advantage is taken of this in preparing many cosmetic emulsions. Usually free fatty acid is incorporated with the oils and waxes, and free alkali is dissolved in the water. Then, at a suitable temperature, the two solutions are brought together. Wherever oil contacts the water, soap will form at the interface, reducing the interfacial tension instantly to an exceedingly low value. Thus a very fine emulsion can be formed without much agitation. If the soap were incorporated as such, much more vigorous agitation,

possibly the use of a colloid mill or homogenizer, would usually be required.

The principle is used widely. In making vanishing creams, the molten stearic acid is mixed with a water solution of the alkali. In making cold creams, a mineral oil solution of the beeswax, which contains free cerotic acid, is mixed with a solution of borax in water. Conventional hand lotions, which are essentially dilute vanishing creams, are made in a similar manner.

Thus the stability of an emulsion may not be predictable by the ease with which the emulsion is formed. If we are primarily concerned with prolonged stability of the emulsion, and if very vigorous agitation can be used in the emulsification procedure, then low equilibrium interfacial tension is of primary interest. If, however, it is essential to emulsify an oil effectively without vigorous agitation, then initial interfacial tension is important. If that value is high, poor results will be obtained no matter how low the final value.

On thermodynamic grounds, surface-active agents of high molecular weight show a stronger tendency to concentrate at oil-water interfaces than low molecular-weight agents of analogous structure and with the same polar-nonpolar balance. However, such high molecular weight agents diffuse slowly and require considerable time to achieve equilibrium interfacial tension at an oil-water interface. The low molecular weight agents reach equilibrium rapidly, but that equilibrium value

may not be low enough for long-term stability of the emulsion. By using a combination of the two types of agent, it is possible to achieve quick effective emulsification and yet high stability. The low molecular-weight agent acts quickly to lower the interfacial tension moderately, and thus helps to disperse and temporarily stabilize the emulsion. On aging, the preferentially sorbed high molecular weight agent largely displaces the other from the interface, thus yielding a very low final tension.

BREAKING AND CREAMING OF AN EMULSION

It is important to distinguish between breaking and creaming of an emulsion. Thus in an O/W emulsion, the oil droplets may actually coalesce and float to the top as a free oil layer. This is breaking. However, the oil droplets will float toward the top even if they do not coalesce. After a time, a clear aqueous layer may be seen at the bottom and a concentrated emulsion cream at the top. This is creaming. Since the emulsion has not broken, it can be redispersed uniformly by very slight agitation. As has been noted, creaming can promote breaking by forcing the droplets into contact with each other. However, if an effective emulsifier is used, the cream may remain unbroken for a long time. If a sufficiently aged emulsion cream is drawn off and allowed to stand, it will show little or no tendency to further creaming. The emulsified

droplets are already packed as closely as possible, approximating the theoretical calculated packing.

Advantage has been taken of this effect to produce unusually stable emulsions by emulsifying 76 per cent of the inner phase with 24 per cent of the outer phase. The point is that close-packed uniform spheres occupy 76 per cent of their containing volume. Of course the 76:24 ratio is not exactly correct, since the droplets are of different sizes and since they can be deformed from their spherical shape under the forces of buoyancy. Nevertheless, emulsions made in this way often show very little or no creaming. An emulsion in which the inner phase is more than about 76 per cent of the total volume is apt to be very stiff, since the droplets are distorted from their spherical shape and can interlock instead of rolling past each other.

COMBINATIONS OF FORCES

It is essential for best results that the physico-chemical and the mechanical factors in emulsification be combined properly. For instance the use of homogenizers or other powerful mechanical disintegrators to form emulsions may actually be harmful if the emulsifying agent is inefficient or insufficient. Many droplets which are uncoated or incompletely coated with emulsifier are formed, and these coalesce rapidly. Less effective agitation would have formed a rather coarse but tolerably stable emulsion. This happens.

On the other hand, if the emulsifier is a very effective stabilizer but does not rapidly yield a low interfacial tension for a freshly formed interface, then the use of the homogenizer or colloid mill may be highly desirable. Otherwise the droplets will not be as fine as they should be, and the emulsion will appear coarse and will tend to cream, if not to separate. In some cases the work can be done physico-chemically instead of mechanically. Combining oils plus free fatty acid with water plus alkali, as discussed, is an example.

USE OF ANTAGONISTIC EMULSIFIERS

It is frequently taught that emulsifiers which form O/W emulsions, for instance soaps and the water-soluble anionic and non-ionic agents, are antagonistic to those which form W/O emulsions, for instance lanolin, cetyl alcohol, and many oil-soluble surface-active agents. The logical conclusion would be that it was always wrong to use such opposed emulsifiers together. That this is not necessarily true is attested by many useful formulas. Although an emulsifier sometimes breaks an emulsion stabilized by an antagonistic emulsifier, it is often found that a limited amount of a correctly chosen antagonistic emulsifier aids in stabilizing an emulsion. This may be due to the formation of a dual interfacial film, with one emulsifier-film more deeply in the water phase and the other more deeply in the oil phase. This would make the transition at the interface

more gradual and would also increase the thickness of the emulsifying layer.

It is therefore not uncommon for limited proportions of lanolin or fatty alcohols such as cetyl or stearyl to be used along with soap or sodium lauryl sulfate in stabilizing O/W emulsions. A combination of an oil-soluble and a water-soluble non-ionic agent is sometimes a better emulsifier than either one alone. One of the largest manufacturers of non-ionic agents recommends use of such combinations in formulas for skin creams, sun-tan lotions, hair dressings, and other cosmetic preparations.

DISPERSION OF SOLIDS

The dispersion of solids will not be discussed in detail. Solid particles, unlike liquid droplets, cannot ordinarily coalesce completely. They can and do group together, under certain conditions, to form loosely attached flocs. It is much easier to break a floc into its constituent particles than to break up the particles themselves. However, to do either is useless if the particles will coalesce into flocs again the moment agitation has ceased. Dispersing agents owe their effectiveness to sorption at the interface between solid particles and liquid, thus preventing the particles from flocculating. Here again it is necessary to integrate the mechanical and the physico-chemical factors or the product will be less satisfactory than desired, and money

will be wasted in useless processing or in useless raw materials.

An interesting aspect of pigments in powders, lipsticks, and other pigmented cosmetics, is that their coloring power increases as they are made finer—up to a certain point—whether subdivision is caused by grinding or by deflocculation. This is true only within limits. Beyond the limit of fine particle size, the coloring power decreases. Particles which are substantially smaller than the wave length of light have no color.

Related to this is the fact that the whiteness of an emulsion is controlled by particle size. If an emulsion is quite coarse, it will be grayish and translucent. As the particle size is made smaller, it will become whiter and more opaque, since more surfaces at which light can be reflected and diffracted are created. However, if the particle size becomes too small, the emulsion will lose whiteness and opacity. The extreme example is a colloidal sol which, like a solubilized liquid, is transparent to transmitted light.

Usually the problem is that the particles are too coarse rather than too fine. So proper milling and deflocculation of such products as lip rouge is important, not only to obtain a uniform product, but to obtain maximum color. Variations in particle size cause differences in shade.

Deflocculation may be important for several reasons. If it is desired to suspend a powder in a liquid, as in calamine lotion or some liquid

make-up preparations, flocculation must be avoided. Otherwise a coarse, unattractive precipitation will occur quickly. The consistency of a paste depends largely on degree of flocculation. Often a very firm paste will break down at once to a liquid or semiliquid when a trace of deflocculating agent is added. These considerations become very important whenever it is desired to obtain a paste of standardized thickness.

CONCLUSIONS

The foregoing discussion has necessarily been incomplete. Important fields of surface chemistry and cosmetic practice have been omitted or mentioned briefly in passing. To those who are not familiar with the science of surface chemistry, the treatment has probably been suggestive rather than informative.

Today, with so many new materials and new techniques available, workers in the field of cosmetic science require at least a working knowledge of the principles of surface chemistry. Without that, one is reduced to wasteful trial and error or dependence on manufacturers' recommended formulas. Particularly is this true for the use of the surface-active agents. In the versatility of the newer non-ionic agents, in the bactericidal action and unusual wetting properties of the cationic agents, in the incompletely explored special properties and synergistic effects of all classes of these agents, lie the unborn cosmetics of the future.