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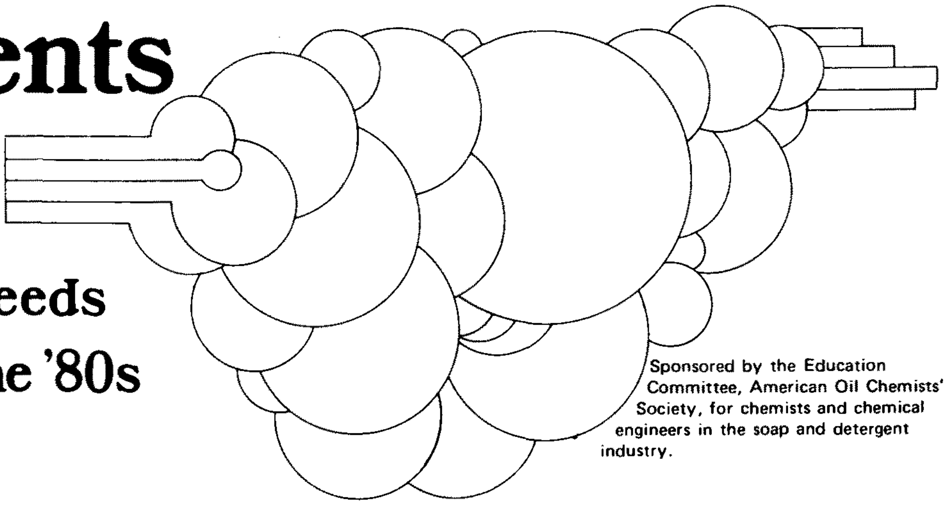

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Session 3

Are Theoretical Surface Chemistry Measurements Really Practical?

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ABSTRACT

The principles and concepts of surface chemistry can be of enormous aid in the application of surfactant chemicals to practical cleaning and foaming problems. The use of surfactants for foam stability was seen to be dependent on rheological properties of the foam (bulk and surface viscosity) and to the energetics of the adsorbed surfactant monolayer (area/surfactant molecule, monolayer elasticity modulus, rate of monolayer spreading and rate of surfactant adsorption into the interface). From these principles, an equation predicting foam volume in the presence or absence of soil was derived and found to be in good agreement with experiment. In detergency, the performance was dictated by the thermodynamic work of adhesion between the soil and substrate. The adhesion was a function of surface properties (soil/water interfacial tension and soil/water/substrate). The role of agitation in detergency was shown to be that energy which was needed to overcome the adhesive bond between soil and substrate. The implicit form of the agitation term was discussed (dependent on substrate configuration, agitator system geometry and mechanics) but not explicitly deduced. The role of interfacial tension was discussed in relation to foam stability and detergency. In both applications, low interfacial tension is beneficial to performance. However, because other surface chemical effects play a role in performance in detergency and foam stability, it was noted that interfacial tension is not the sole correlating parameter with performance. The situations in which low interfacial tension is not sufficient to give improved detergency and foam stability performance were delineated. A possible new method of aiding in optimizing oil/surfactant performance also was discussed. Finally, the role of micelles in detergency was examined in light of very recent experimental work which suggests that micelles may be detrimental to detergency and foam stability performance. This study suggests that surfactants which form mesomorphic phases with soil give better performance. Micelles, instead of solubilizing soil in their hydrophobic cores, are said to be competing with the mesomorphic phase formation process, thereby hindering detergency performance. It is suggested by the sheer weight of new theoretical and innovative approaches to surface chemistry applied to detergency and foam stability performance that "theoretical surface chemistry measurements really (are) practical!"

INTRODUCTION

In the technological world of 1980, applications of surface chemistry to the quality and style of life are ubiquitous. This, then, invokes the question, expressed in the title of this paper, as to whether theoretical surface chemistry investigations are a necessary and worthwhile undertaking. As a general answer to this question, a quote from Schwartz (1), in reference to a similar question on the subject of detergency studies, seems appropriate: ". . . the methods we now regard as 'practical' were originally conceived as being (theoretical) research methods." From such a statement, one deduces that application derives from theory so that the two are, in effect, chronologically continuous elements of the technological process. It is from this viewpoint that this paper is directed. Specifically, the theories of capillarity and surface chemistry are applied to the phenomena of detergency and foam stability. A short history on the theoretical work in each area is given, but emphasis is on current theories with experimental results where possible.

EXPERIMENTAL

The apparatus used to measure foam stability was a modified Schlag apparatus, as shown in Figure 1. For this study, 200 ml of deionized water plus 150-ppm synthetic hardness (Ca and Mg chlorides) were added to each cylinder. Then 40 ml of a 0.3-wt/wt % aqueous surfactant solution were added to each tube, and care was taken to not cause foaming. The aqueous surfactant solutions were commercial-type light duty liquid (LDL) detergents, which are nominally 30% active. Therefore, the surfactant solutions were 0.3% "as is," but nominally 0.1% active.

The tubes containing 240 ml of surfactant solution then had varying amounts of soil added to simulate dishwashing experience. The soil was a Safeway product, Keen, which is a hydrogenated vegetable shortening, solid at room temperature and containing no dispersing agents found in many other commercial shortenings.

The graduated cylinders were placed in the water bath and thermostated for 10 min. Then the plunger/agitator was turned on for 50 strokes at the rate of ca. 1 stroke/sec. At the end of 50 strokes, the plunger/agitator was stopped in the "up" position and the foam volume was measured immediately. The foam volume (excluding the bulk aqueous phase volume) was recorded.

Commercial formulations were not used. All formulations were mixed from individual components to produce formulations similar to those commercially available. The linear alkyl sulfonate (LAS) used was Conoco C-550. The alcohol ether sulfate (AES) was a Conoco lab-prepared sample. The lauric myristic ethanolamide (LMMEA) was a commercial product, P621, from Stepan Chemical Co.

DISCUSSION

Foam Stability

Previous studies. Foam stability in detergency systems is an important property in two major surfactant applications: dishwashing detergents and hair shampoos. Many parts of this paper may be applicable to other foam stability applications (i.e., toothpaste, food applications), but the subject matter will be directed specifically at dishwashing detergents and hair shampoos.

Foam studies generally are of two types: (a) static (foam stability of drainage), and (b) dynamic (foam generation or height). However, the multitude of tests which fall in one or both of these two classes generally are applications-oriented and are not based on fundamental physical properties of foams and aqueous surfactant solutions. For a description of many of these tests, the reader is referred to review articles on the subject (1-3).

A few researchers have attempted to examine the fundamental aspects of foam behavior (1,2,4,5,6). However, most of these studies have not produced results of practical utility, and rarely is soil considered in the more fundamental work. Thus, the state of the art is best summarized by Adamson (5): "In conclusion, there does not seem to be any rigorous analysis possible of the interrelation of factors determining foam stability." The purpose of the following presentation is to introduce or reintroduce some of the fundamental properties of foam and foam stability and then to develop from a rigorous thermodynamic treatment an expression for application to practical foam stability systems in the presence and absence of soil.

Mechanism of Foam Stability

For purposes of this paper, foam stabilization mechanisms will be divided into two separate categories: electrostatic (DLVO) and nonelectrostatic. (Foam stability can also be enhanced by the presence of significant quantities of small solid particles [7,8]. However, this presentation will include only foam stabilization by molecularly dispersed additives.) In the first category, the electrostatic stabilization by double-layer repulsion has been explained well on the basis of the DLVO (Derjaguin, Landau, Vervey, Overbeek) theory (9-13). In brief, this theory predicts the amount of stabilizing potential energy imparted to a foam bubble or double-layer thin film as a function of electrolyte charge, electrolyte concentration, film thickness, liquid dielectric constant and liquid viscosity. The theory has been very successful in predicting the extra potential energy of stabilization for foams upon the addition of electrolytes. The only limitation to this theory is the experimental difficulty in measuring the interfacial potential and the

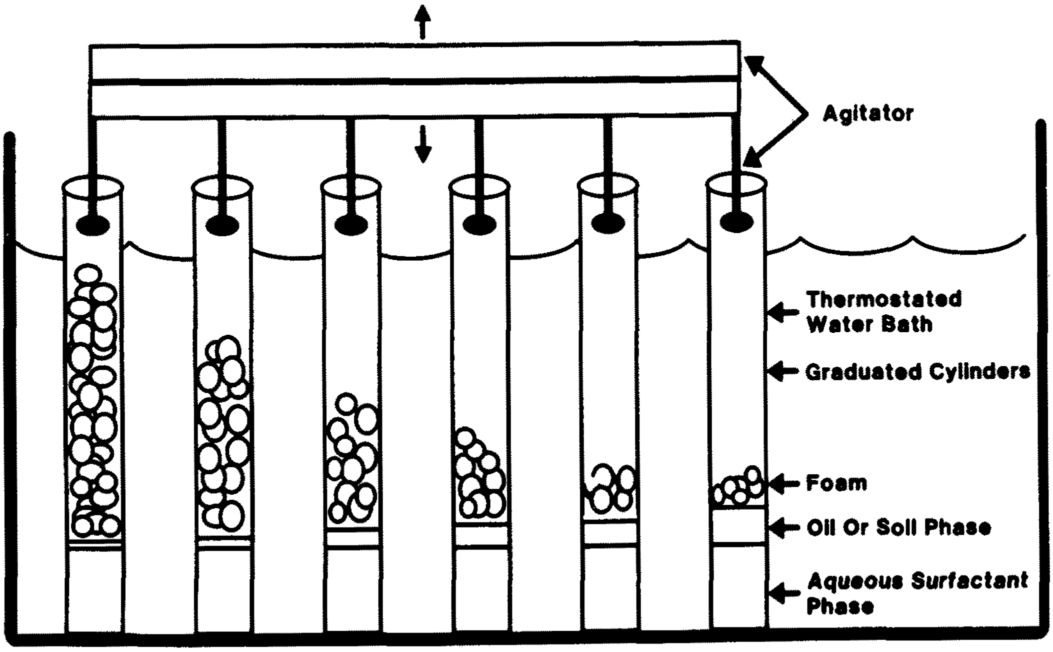

FIG. 1. Schlag foam stability apparatus.

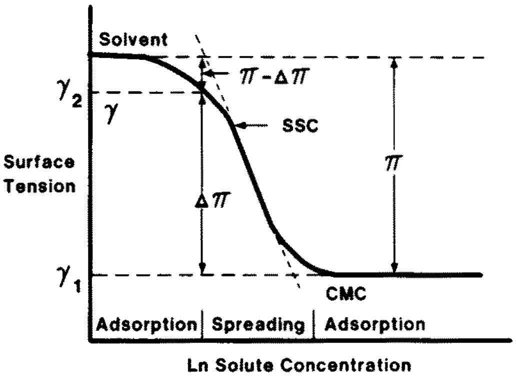

FIG. 2. Mechanical model of the components of foam stability.

Hamaker Constant. The rudiments of the DLVO theory for foam stability by electrostatic double-layer repulsion are discussed in Appendix I.

The mechanism of foam stabilization by nonelectrostatic means is a complicated process that is dependent on numerous physicochemical properties of the foam system. For this reason, most discussions of the subject describe individual aspects of nonelectrostatic foam stability without describing how they simultaneously interact. Therefore, an attempt will be made to delineate the components of nonelectrostatic foam stability and then integrate these parts into a comprehensive mechanism.

One of the better overviews on the subject of nonelectrostatic foam stability was given by Davies and Rideal (14). The mechanical factors working to stabilize an aqueous surfactant thin film or bubble surface are schematically depicted in Figure 2.

Consider an aqueous surfactant solution with a foam layer and a bulk phase surfactant concentration sufficient to give a surface tension of γ_1. Each bubble surface will have a surface tension of γ_1. Now, let a bubble surface be mechanically disturbed, as shown in Figure 3a. The disturbed area will have an increased surface area due to the thinned monolayer of γ_2. There will then be a film pressure of γ_1-γ_2 or $\Delta\pi_{12}$ acting to push surfactant molecules from the region of γ_1 into the depleted region of γ_2. This behavior is often referred to as the Marangoni Effect (14-16). This spreading process carries bulk aqueous phase into the disturbed area along with the surfactant monolayer molecules, so the film thickens as shown in Figure 3b. Then, eventually, as shown in Figure 3c, the film returns to its original, undisturbed configuration with thickness λ. This process is strongly influenced by bulk and surface viscosities, but for typical surfactant systems, the complete process of Figures 3a through c occurs in milliseconds (17).

Alternatively, the same aqueous system as just described could have a surface tension γ_1 as shown in Figure 4a, but undergo a longitudinal stretching, which diminishes its thickness λ and gives a new surface tension γ_3. In such a case, there is no monolayer phase to spread over the depleted surface. As a result, there is no pressure differential in the surface phase. Instead, stability is maintained only because surfactant in the bulk inner layer diffuses rapidly to the surfaces.

Thus, two mechanisms (monolayer spreading and adsorption from the bulk) work to stabilize any distended film or bubble surface. The mechanism which predominates will be the more rapid of the two. That is to say, the greater of $\dot{\pi}_{SPR}$ or $\dot{\pi}_{ADS}$ will determine which foam stabilization mechanism is operative. As shown in Figure 2, the spreading mechanism should be predominant where the monolayer is present, but bulk phase surfactant concentration is neither large nor small. At high bulk phase concentrations, surfactant can replenish the interface before a monolayer can respread over a disturbed film area. Inversely, at low bulk phase concentration, insufficient adsorbed surfactant exists to even form a monolayer; in this case, diffusion varies with concentration whereas π-$\Delta\pi$ varies with ln concentra-

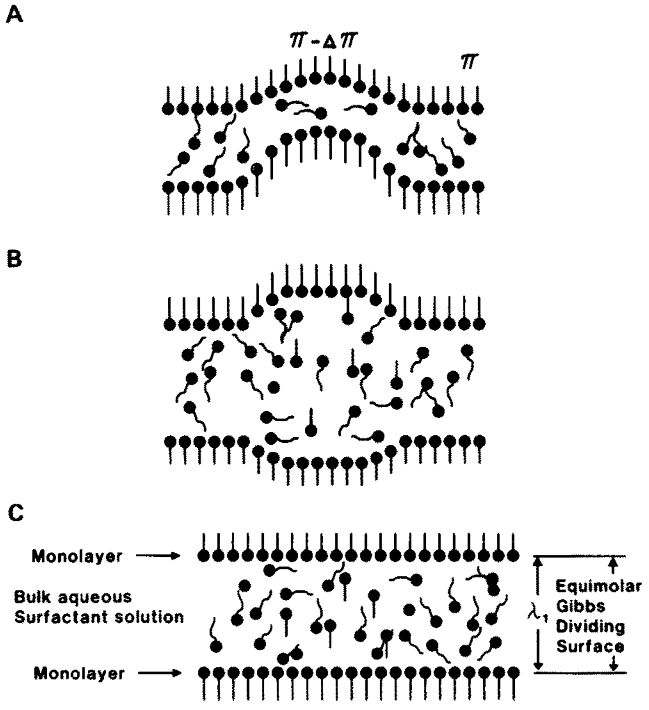

FIG. 3. Surfactant film stabilization by monolayer spreading (Marangoni Effect): (a) mechanical instability; (b) thickened film; (c) equilibrium film.

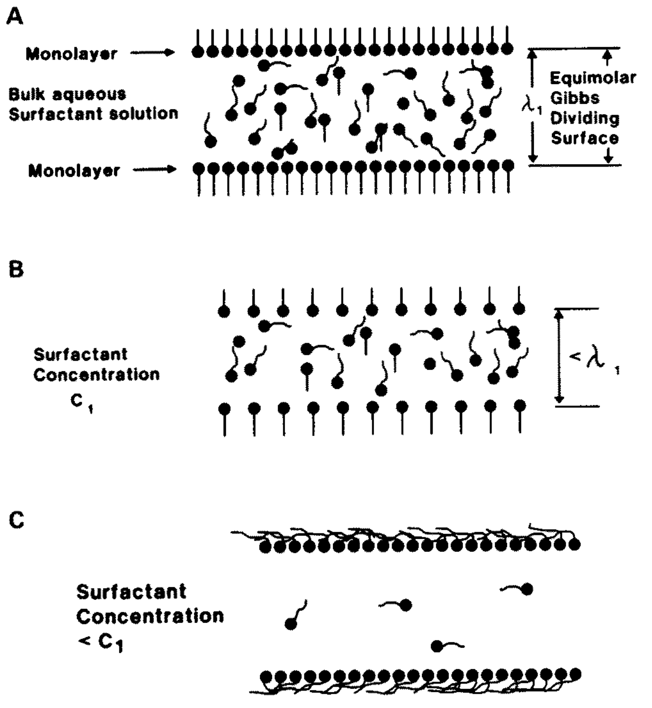

FIG. 4. Surfactant film stabilization by adsorption: (a) equilibrium film; (b) instantaneously extended film; (c) equilibrium extended film.

tion, so diffusion outstrips monolayer flow. Also in Figure 2, the effect of changing surface viscosity μ_S is shown. A decreasing surface viscosity causes a corresponding widening of the concentration range over which the spreading mechanism of foam stability predominates. However, surface viscosity only works to retard the monolayer flow. The driving force for monolayer flow is the spreading pressure $\Delta\pi$. In defining this quantity, the last important factor affecting foam stability arises.

When the molecules in a stretched interface go from an area/molecule in a monolayer $\bar{A}_M$ to a larger area/molecule of $\bar{A}$, the film pressure $\Delta\pi$ will be:

$$\Delta\pi = -\left(\frac{\partial\pi}{\partial\bar{A}}\right)(\bar{A} - \bar{A}_M) \qquad [I]$$

Rearranging Equation I gives:

$$\Delta\pi = -\bar{A}_M\left(\frac{\partial\pi}{\partial\bar{A}}\right)\left(\frac{\bar{A}}{\bar{A}_M} - 1\right) \qquad [II]$$

or

$$\Delta\pi = E\left(\frac{\bar{A}}{\bar{A}_M} - 1\right) = E\,(\bar{A}_r - 1), \qquad [III]$$

where E is, by definition, the surface elasticity modulus (5,14,18). The quantity E is a measure of the monolayer's affinity to spread.

At this point, all the variables which are currently recognized as influencing nonelectrostatic foam stability have been introduced and can be written as:

$$\underset{\text{(nonelectrostatic)}}{\text{Foam Stability}} = f\,(\mu_S, \mu, \bar{A}_r, E, \dot{\pi}_{SPR}, \dot{\pi}_{ADS}) \qquad [IV]$$

The quantity μ is the viscosity of the bulk aqueous phase. This quantity plays more of a role in destabilizing the foam through drainage. However, our discussion is aimed more at foam stability as it applies to the amount of foam which is generated and is stable for a period of time (say 1 min after agitation stops) before significant foam breakage occurs due to drainage. Foam breakage studies which look at long-term stability are generally considered kinetic studies (5,19-21), whereas the foam stability tests which measure foam volume shortly after generation are steady-state or equilibrium tests. As pointed out by Bikerman, foam drainage and foam stability are different mechanisms (20).

Using the foregoing discussion, it will now be possible to develop a concise mathematical concept for foam stability in an air/oil/aqueous surfactant system. In addition, the previous analysis will allow an assessment of the scope and applicability of such a mathematical result.

Thermodynamic Treatment of Foam

Stability. The model for either a dishwashing or shampoo foam stability is shown in Figures 4a-c. The process is envisioned as an aqueous surfactant solution which initially has a total bubble surface area A_i until a soil or oil phase is added. The oil absorbs from the aqueous phase its saturation concentration of surfactant, thereby reducing the surfactant available for foam stability and creating a smaller total bubble surface area A. In Appendix II, an equation for surface area changes resulting from soil introduction is derived as:

$$\frac{A}{A_i} = \left(\frac{V_W}{V_W + k_s^{o/w} V_o}\right)^{\frac{RT}{\bar{E}}} \qquad [V]$$

Several observations about Equation V are notable. The expression in parenthesis will give a smaller area ratio (A/A_i) as the surfactant becomes more oil soluble (i.e., as $k_s^{o/w}$ increases). Also, the exponent is an energy ratio of kinetic (RT) to elastic ($\bar{E}$) energies. Thus, the greater the molar surface elasticity modulus ($\bar{E}$), the smaller the exponent, and hence, the slower the amount of foam decreases with increasing soil load. These predictions by Equation V are qualitatively consistent with foam stability behavior.

Experimental Results

In Figures 5 through 7, Equation V is compared quantitatively with experimental results using a Schlag instrument (described in Experimental) to generate foam height in the presence of varying amounts of soil. The experimental results give exponent values ($RT/\bar{E}$) of 1 to 10 dynes/cm. In order to interpret these results, one should note that lower exponents indicate better foam stability because the greater exponent corresponds to a greater elasticity modulus $\bar{E}$. Therefore, Figures 5 through 7 indicate that the high LAS commercial formulation (Fig. 6) gives the best foam stability, whereas the low LAS commercial formulation (Fig. 7) and the neat LAS formulation (Fig. 5) give similar, but lower, foam stability. This experimental result is consistent with dishwashing tests which also show that high LAS commercial LDL formulations give the best foam stability.

One feature of Equation V is that only relative foam quantities (i.e., A/A_i) need to be measured. However, should absolute foam quantity be desired, one need only determine A_i. The quantity A_i (also $\bar{E}$) will vary with changes in hardness, foam stabilizers/breakers, surfactant type, surfactant concentration and other factors. For an excellent discussion of foam area calculations, see ref. 6.

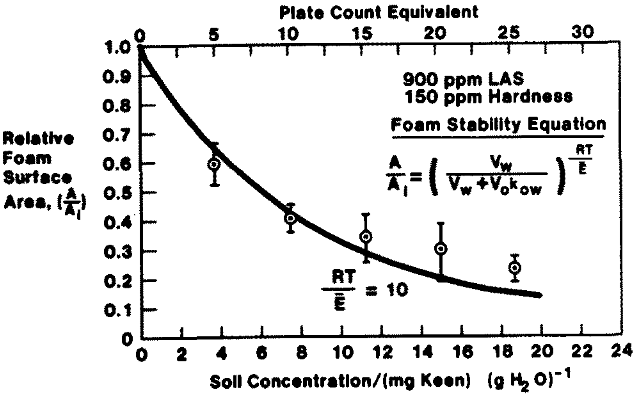

FIG. 5. Foam stability in the presence of soil for LAS.

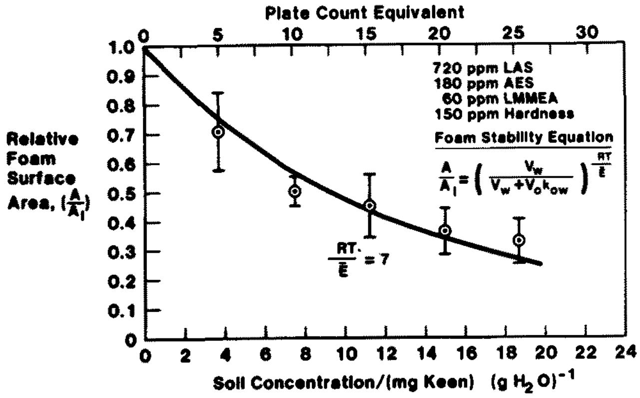

FIG. 6. Foam stability in the presence of soil for commercial-type LDL formulation.

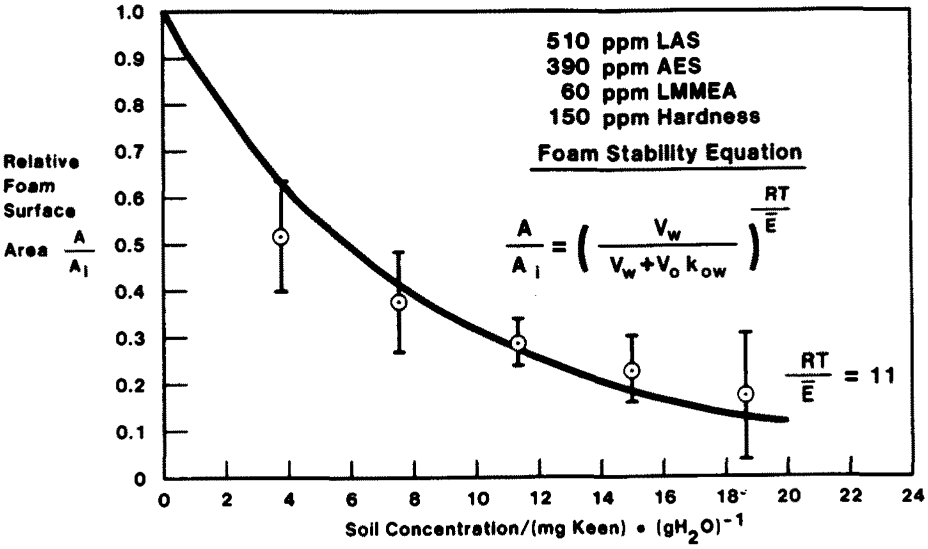

FIG. 7. Foam stability in the presence of soil for low LAS commercial-type LDL formulation.

DETERGENCY

Previous Studies

The process of removing soil from a substrate in an aqueous solution by mechanical and chemical means has a history which precedes recorded history. More recently, the commercial availability of synthetic detergents has replaced soap, the original detergency agent. Good review articles on different detergent types are readily available (12,22,23). Moreover, methods for measuring detergency are numerous and are continuing to evolve, as noted in review articles on the subject (1,24-27). Alternatively, though, the fundamental principles of detergency are invariant. However, from review articles covering theories on detergency (28-36), we find that different authors have varied opinions as to the basic mechanisms of detergency. Furthermore, this disunity obscures the relationship between fundamental detergency principles and their relationship to detergency applications. The challenge, then, to the researcher, is to identify and then apply these fundamental principles to the very practical problems of soil removal and to provide better detergent and detergency measurement systems. This challenge requires ambitious pursuit. The following paragraphs will seek only to identify the basic components of detergency and then suggest how much information can be applied to improving detergency.

Thermodynamic Treatment of Detergent

The detergency process begins with an unwanted soil adhering to a solid substrate. For now, it will not be necessary to specify whether the soil is solid or liquid or whether the substrate is fibrous or macroscopically flat. The process of detergency is shown diagramatically in Figure 8.

The soiled solid (fabric or hard surface) and the aqueous surfactant represent the initial system of interest, with a combined free energy of G_{INIT}. The next step is to immerse the soiled solid into the aqueous surfactant producing the free-energy state G_{IMM}. Upon immersion, the three phases (soil, solid and aqueous surfactant) begin to interact through absorption and adsorption until an equilibrium free-energy state G_{EQ} is reached. At this point, equilibrium soil removal would result in a clean solid surface, free-energy state G_{CLN}. Now, viewing these

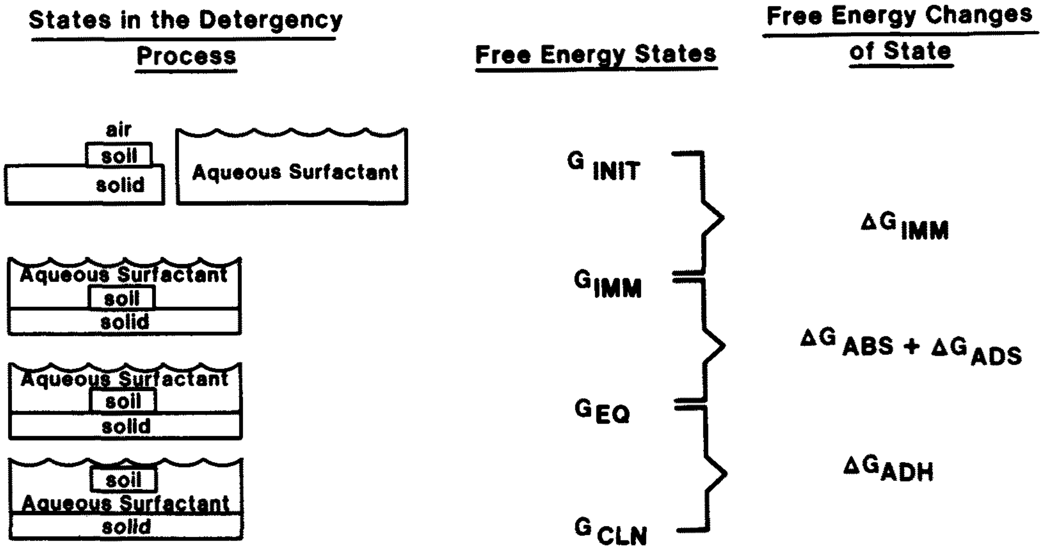

FIG. 8. Representation of the free-energy process of soil removal.

free-energy states in a thermodynamic sense, we know that no energy state can be determined; only energy state differences. For our purposes here, this apparent limitation has a dual benefit because it is the free-energy changes which correspond to detergency processes, with the free-energy states serving as well-defined standard states.

The first three energy processes, ΔG_{IMM}, ΔG_{ABS}, and ΔG_{ADS}, will be discussed simultaneously because, although they are three distinctively different processes in a thermodynamic sense, they occur simultaneously in practice. Upon immersion of a soiled solid in an aqueous surfactant solution, two interfaces are destroyed (soil/air and solid/air) and replaced by two others (soil/aqueous and solid/aqueous). This process is viewed as contact between these surfaces without rearrangement of the surface atoms ΔG_{IMM}, then allowing rearrangement, and hence, adsorption at the interfaces ΔG_{ADS}, and finally, mutual miscibility of bulk phases, including mesomorphic phase formation ΔG_{ABS}. The interested reader is referred to Harkin's excellent monograph (37) on this process for further details. However, for our purposes, this paper will proceed to the last process which is of primary interest in detergency, as will become apparent shortly.

Once the immersed, soiled solid has reached equilibrium among all the phases and interfaces, the process of interest, i.e., soil removal, can be treated. When the soil is removed by any physicochemical method by an equilibrium path, the process energy required is the free energy of adhesion ΔG_{ADH} for the soil and solid in equilibrium with the aqueous phase. For this process, a soil/aqueous and solid/aqueous interface are created with interfacial tensions γ_{OW} and γ_{SW}, respectively. Also, a solid/soil interface with interfacial tension γ_{SO} is eliminated. Therefore, one can write a free-energy balance for the process ΔG_{ADH}, which, by definition (38), is the work of adhesion W_{ADH} or

$$\Delta G_{ADH} = W_{ADH} = \gamma_{OW} + \gamma_{SW} - \gamma_{SO} \qquad [VI]$$

Equation VI expresses the free energy of adhesion between a soil and a substrate. Alternatively, W_{ADH} is the work required to remove soil. If the soil is liquid, it will have a contact angle θ with the solid. As shown in Figure 9, the interfacial tensions of a soil/solid/aqueous phase system can be expressed in relation to θ through the Young-Dupre equation

$$\gamma_{SO} = \gamma_{SW} + \gamma_{OW} \cos\theta \qquad [VII]$$

Combining Equations VI and VII gives

$$W_{ADH} = \gamma_{OW}(1 - \cos\theta) \qquad [VIII]$$

Equation VIII also expresses the energy required for soil removal, but the variables in Equation VIII are fewer and simpler to evaluate experimentally than γ_{SO} and γ_{SW}. Furthermore, Equation VIII provides the limiting criterion for soil removal to be ascertained. For surfactants which make W_{ADH} go to zero, soil removal is spontaneous, thus requiring no agitation. For the case in which $W_{ADH} = 0$, this can occur if γ_{OW} has become zero or if θ becomes zero. (Actually, $W_{ADH} = 0$ if both γ_{OW} and θ are zero, but this is the primitive case in which both mechanisms operate simultaneously.) In the case of no interfacial tension, spontaneous emulsification occurs and the soil is solubilized either by direct dissolution or by going through a mesomorphic stage prior to dissolution. The latter case is that of "roll-up," as can be seen by Figure 9. Therefore, the detergency process can be summarized in the following two equations: for solubilization, emulsification, $\gamma_{OW} = 0$, and for roll-up, $\theta = 0^\circ$. This information deserves a few comments. In most theoretical treatments of detergency, W_{ADH} or ΔG_{ADH} is confused with other free-energy processes given in Figure 8. While these processes play an important role through adsorption and absorption of surfactant in/on the soil and solid substrate, they are distinct from the adhesion process. Many of the classifications of soil removal described by other authors as distinct soil removal mechanisms (i.e., emulsification, solubilization, mesophase formation are more properly classed as adsorption and absorption behavior. The work of adhesion depends only on the values of γ_{OW} and θ, which result after miscibility equilibrium for all phases has been achieved.

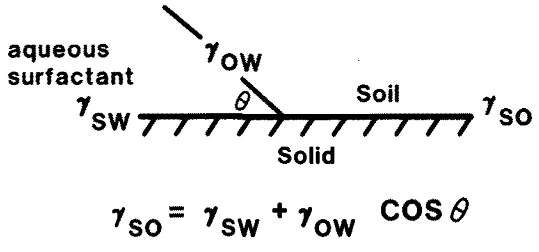

FIG. 9. The Young-Dupre equation in detergency: soil/substrate adhesion.

On the other hand, when particulate or solid soil is present, θ in Equation VIII loses its meaning. Equation VI remains valid but all of the interfacial tensions are experimentally very difficult to measure. An alternative approach for determining W_{ADH} for particulate soil would be the DLVO (9-13) procedure. A discussion of this procedure is given in Appendix I (9-13).

Finally, in most real detergency systems, W_{ADH} is small, but not zero. Therefore, soil removal will not be spontaneous. Instead, soil removal is achieved in a duplex manner of first lowering W_{ADH} as much as possible with surfactants, and second, overcoming the remaining adhesive bond between the soil and cloth with mechanical energy or work of agitation W_{AGIT}. In this way, soil removal is achieved when the sum of W_{ADH} and W_{AGIT}, defined as the work of detergency W_{DET}, becomes 0. The condition for soil removal can be expressed in equation form as

$$W_{DET} = W_{ADH} + W_{AGIT} \leqslant 0, \qquad [IX]$$

where $W_{AGIT} \leqslant 0$ by thermodynamic convention of "work in" being negative.

The explicit form of W_{ADH} has been given in Equations VI and VIII. The explicit form of W_{AGIT} currently is not known. Implicitly, it must be functionally dependent on such factors as (a) substrate configuration (i.e., fiber, flat solid, porous solid), (b) agitation energy input, (c) geometry of the agitation system, and (d) physical properties of aqueous phase. Defining and quantifying the role of agitation in detergency is a topic which should receive extensive study in the future.

PERFORMANCE OPTIMIZATION WITH INTERFACIAL TENSION

In the preceding sections, the surface chemistry rudiments of foam stability and detergency were examined. From these analyses, the role played by surface or interfacial tension γ in the foam stability and detergency performance was rather cursorily discussed. However, because γ is such a familiar and easily measured surface chemical property, it seemed reasonable to reverse the discussion order and examine γ as a function of foam stability and detergency performance instead of vice versa.

In detergency, W_{ADS} was a product of γ_{OW} and cosine θ. Because the goal in performance improvement in detergency is to make W_{ADS} as small as possible, it is logical that reducing γ_{OW} by proper surfactant choice is the key.

Lowering γ_{OW}, however, must not be done at the expense of raising cosine θ, or no gain in performance will be realized. As γ_{OW} and θ are not mutually independent in a detergency system, it is instructive to examine their relationship by rearranging Equation VII to read:

$$\cos\theta = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}} = \frac{\tau_{ADH}}{\gamma_{ow}} \qquad [X]$$

By Equation X, one sees that reducing γ_{OW} will increase cosine θ if the adhesion tension τ_{ADH} remains constant. However, in practice, changing a surfactant will change all three interfacial tensions in a generally unpredictable manner. Moreover, τ_{ADH} is experimentally very difficult to obtain independent of θ and γ_{OW}. Therefore, relying on values of γ_{OW} exclusively as a criterion for detergency performance can be tenuous. However, nature is generally kind, in that surfactants which lower γ_{OW} also lower cosine θ. On the other hand, surfactant systems which give ultralow oil/aqueous phase interfacial tensions of $<10^{-3}$ dynes/cm recently have been reported (39) through work in the field of tertiary oil well recovery research. Equally important is the fact that the technology for achieving these low interfacial tensions is available (40). After all, if γ_{OW} can be reduced to zero, spontaneous oil emulsification of the oil into the water occurs and the value of θ to detergency performance is moot.

Briefly, the ultralow tension between an oil and aqueous phase is found to occur when the average molecular weight of the oil is matched to the equivalent alkane carbon number (EACN) of the surfactant. The oil and surfactant can be homolog mixtures of many different molecular species, but whenever an oil contacts an aqueous surfactant phase with the proper EACN, a minimum tension occurs. Currently, work is only beginning to adapt this technology to detergency and foam stability applications; however, such a procedure holds great promise.

For foam stability, ultralow surface tensions are the optimization criterion also, but for a very different reason. In Figure 2, it was pointed out that $\Delta\pi$ was the stability driving force behind the monolayer spreading mechanism. From Figure 2, it is clear that the smaller the value of γ, the larger $\Delta\pi$ will be for any extension of the film or bubble surface. As a result, lower γ (greater $\Delta\pi$) will cause insults to the bubble films to heal more quickly and hence enhance the foam stability. Therefore, surfactants which lower surface tension should improve foam stability as long as the other factors in foam stability given in Equation VI are held constant.

ROLE OF MICELLES IN DETERGENCY AND FOAM STABILITY

No discussion of surface chemistry, either fundamental or applied, would be complete without a discussion of micelles, particularly in aqueous detergency for which classical concept for soil removal has been one of oil solubilizing in the hydrophobic interiors of hydrophilic micelles. However, this view recently has been critically questioned (35,41). The basis for these arguments can be seen in Figure 10. Detergency performance begins at low surfactant concentration. By the time micelles appear (CMC), detergency performance is nearly at its maximum. On the other hand, interfacial tension and monomer concentration have behaviors that inversely or directly correlate with detergency performance, respectively. In addition, recent experimental work (41) has presented other evidence that not only do micelles not aid in detergency, but that micelles might actually be detrimental to detergency performance. The argument is that micelles tie up aqueous surfactant that is needed in the monomeric state in the aqueous phase to achieve detergency. Instead, these authors conclude that surfactants which more readily form mesomorphic phases in conjunction with the soil are the optimal surfactants. This study is the first of its kind to actually find experimental evidence that micelles apparently do not aid in detergency. The ramifications of such a result are intriguing. Alternatively, the onset of micelle formation (i.e., the CMC) may be an indication of aqueous phase changes in energetics or structure which does correlate with detergency (42). Therefore, the significance of micelles in the detergency process is currently one of controversy and should certainly attract a great deal of theoretical and applied research in the near future.

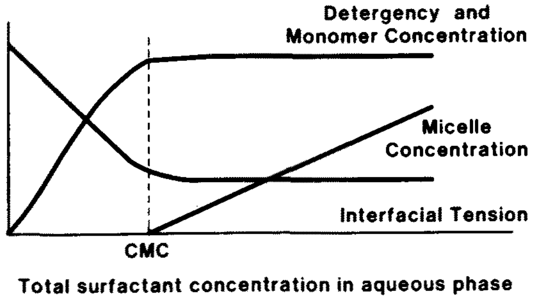

FIG. 10. Qualitative diagram of detergency and related surface physicochemical properties.

APPENDIX I

Electrostatic Adhesion between Solid Soils and Substrates

When particulate soil is present, θ in Equation VIII loses its meaning. Equation VI, however, is still valid for particulate soils but all of the interfacial tensions are very difficult to evaluate experimentally. Instead, the adhesive work in such systems is more readily treated by a DLVO (Derjaguin, Landau, Vervey, Overbeek, 9-13) potential energy approach. A diagram showing the significant features for a charged particle is given in Figure 11. For a spherical (solid) soil particle adhering to a plane solid surface, the potential energy of attraction V (ergs/cm^2) is equal to the sum of electrostatic interaction V_E and the London-van der Waals attraction V_A or

$$V = V_E + V_A \qquad [I\text{-}1]$$

The forces can be written (12,43)

$$V_E = \epsilon\alpha\psi_0^2 \ln(1 + e^{-\kappa x}) \qquad [I\text{-}2]$$

and (44)

$$V_A = -\frac{A}{6x}, \qquad [I\text{-}3]$$

where ϵ = dielectric constant of solvent; α = solvent polarizability; ψ_0 = interfacial potential; κ^{-1} = Debye-Huckel ionic atmosphere radius (45); A = Hamaker constant; a = particle radius; x = distance separating particle and substrate.

Equations I-1, 2 and 3 combine to give the interaction energy curves shown in Figure 12. In this figure, one notes that, at large distances, an attractive interaction occurs at S, but that electrostatic repulsion soon occurs at lesser distances. At ζ, the maximum repulsion, designated as the "zeta potential," occurs but at only slightly closer distances, the potential becomes attractive due to short-range London-van der Waals attraction. This minimum is very deep so that mere agitation is rarely sufficient to remove particulates, especially smaller particles. However, this minimum is very narrow because Born repulsion overwhelms the London-van der Waals forces when atomic distances of separation are reached.

Thus, the DLVO theory is applicable to particulate soil removal, and the only drawback to the application of this theory to particulate detergency is the measurement of certain parameters (A, α and ψ_o) and the fact that particles are not all spherical and surfaces are not all planar, so geometry makes Equations I-1 through 3 only approximate for applied detergency systems.

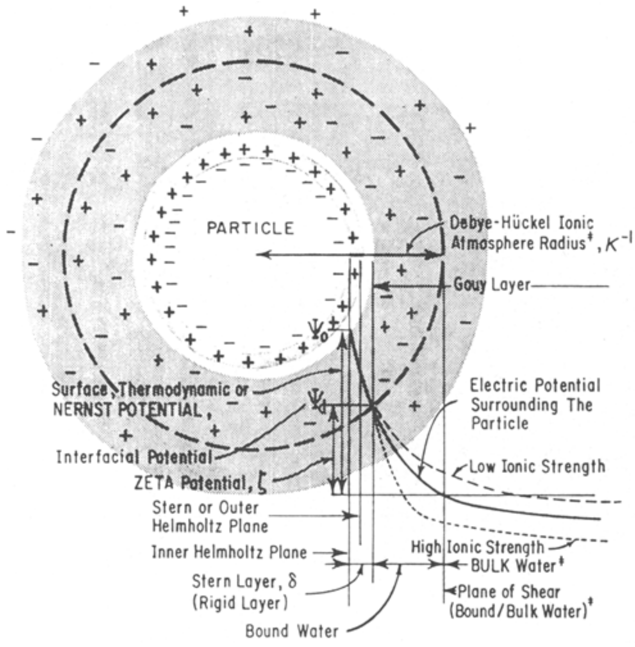

FIG. 11. DLVO model of a charged particle in an aqueous electrolyte solution.

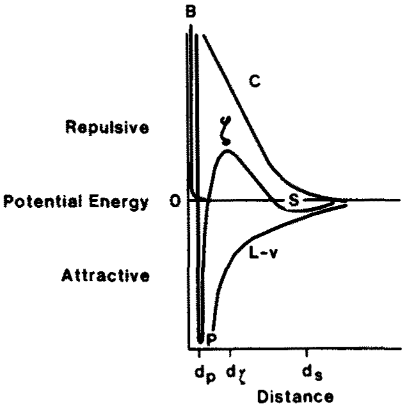

FIG. 12. Derjaguin-Landau-Vervey-Overbeek electrostatic interaction model.

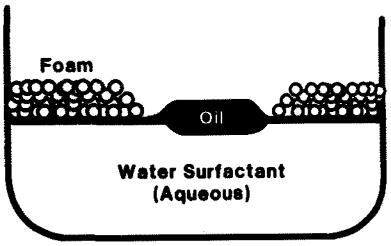

FIG. 13. Schematic model of foam stability test system with soil (oil) present.

APPENDIX II

Derivation of Thermodynamic Foam Stability Theory

To model the foam stability system shown in Figure 13, one begins with the thermodynamic equation for the differential surface excess Gibbs free-energy dG^σ as (46-48):

$$dG^\sigma = -S^\sigma dT + \pi dA^\sigma + \sum_{i=1}^{N} \mu_i \, dn_i^\sigma, \qquad \text{[II-1]}$$

where S^σ = surface excess eutrophy; T = absolute Kelvin temperature; γ = air/aqueous surface tension; A^σ = air/aqueous surface area; μ_i = chemical potential of ith component; n_i^σ = surface excess moles of ith component; N = number of components in aqueous phase.

In applying Equation II-1 to the problem of interest, the Gibbs' formalism of zero solvent (Component 1) adsorption at the interface (viz., $n_1^\sigma = 0$ or the equimolar dividing surface for the solvent) will be adopted (48-49). In addition, Gibbs' concept of treating all the remaining solutes as a single component (50) will be applied to Equation II-1, yielding

$$dG^\sigma = -S^\sigma dT + \pi dA^\sigma + \mu dn^\sigma, \qquad \text{[II-2]}$$

where μ = chemical potential of all solute molecules taken collectively; n^σ = number of moles of solute molecules in the air/aqueous phase interface at the solvent equimolar dividing surface.

From Equation II-2, a Maxwell relation can be written as:

$$\left(\frac{\partial \pi}{\partial n^\sigma}\right)_{T,A^\sigma} = \left(\frac{\partial \pi}{\partial A^\sigma}\right)_{T,n^\sigma} \qquad \text{[II-3]}$$

Then, noting that

$$dn^\sigma = A^\sigma d\Gamma_{(1)} = A^\sigma \Gamma_{(1)} d \ln \Gamma_{(1)}, \qquad \text{[II-4]}$$

and

$$d\mu = RT \, d \ln \overline{C}, \qquad \text{[II-5]}$$

where $\Gamma_{(1)}$ = Gibbs surface excess adsorption of surfactant formulation at the equimolar dividing surface for the solvent (Component 1), and $\overline{C}$ = molar surfactant concentration of surfactant formulation,

$$\sum_{i=2}^{N} \overline{C}_i$$

Equations II-3 through 5 can be combined to give

$$\frac{1}{\Gamma}\left[\frac{\partial \pi}{\partial \ln \Gamma}\right]_{T,A^\sigma} = RT\left[\frac{\partial \ln \overline{C}}{\partial \ln A^\sigma}\right]_{T,n^\sigma} \qquad \text{[II-6]}$$

where subscript on $\Gamma_{(1)}$ has been dropped.

The RHS can be regarded as a surface elasticity modulus E (or molar surface elasticity modulus $\overline{E}$), since

$$\overline{E} = \frac{E}{\Gamma} = \frac{1}{\Gamma}\left[\frac{\partial \pi}{\partial \ln \Gamma}\right]_{T,A^\sigma} = \left[\frac{\partial \pi}{\partial \Gamma}\right]_{T,A^\sigma} \qquad \text{[II-7]}$$

The quantity E is similar to the Gibbs elasticity modulus (51), the surface area elasticity (52), and the surface compressional modulus (53). However, the invariants T and A^σ in Equation II-7 make the modulus $\overline{E}$ significantly different than the three already mentioned. A more complete examination of surface moduli will be examined elsewhere (54).

Combining Equations II-6 and II-7 gives

$$\left[\frac{\partial \ln \bar{C}}{\partial \ln \bar{A}^{\sigma}}\right]_{T,n^{\sigma}} = \frac{\bar{E}}{RT} \qquad [II\text{-}8]$$

Equation II-8 can now be put in integral form as

$$\int d \ln A = \frac{RT}{\bar{E}} \int d \ln \bar{C} \qquad [II\text{-}9]$$

under conditions of constant T and n^{σ}. Now consider an aqueous foam system in which a recently generated foam of total surface area A_*^{σ} suddenly has a water-insoluble oil phase dispersed throughout. An example of such a case would be dishwashing, in which plates containing an oil phase (soil) are added to a pristine foam system. Upon reaching equilibrium, the oil will extract an amount of the surfactant, thereby causing the initial foam bubble surface area to decrease from A_*^{σ} to A^{σ} with a corresponding decrease in water phase surfactant concentration from $\bar{C}_{s*}^{w}$ to $\bar{C}_s^{w}$. If Equation II-9 is integrated over these limits and then simplified, the result is

$$\frac{A^{\sigma}}{A_*^{\sigma}} = \left(\frac{\bar{C}_s^{w}}{\bar{C}_{s*}^{w}}\right)^{\frac{RT}{\bar{E}}} \qquad [II\text{-}10]$$

To put Equation II-10 into a more useful form, one must first quantify the surfactant extraction capacity of the oil with the oil/water surfactant distribution coefficient $k_s^{o/w}$ as

$$k_s^{o/w} = \frac{\bar{C}_s^{o}}{\bar{C}_s^{w}} \qquad [II\text{-}11]$$

Second, alternative expressions for $\bar{C}_s^{o}$, $\bar{C}_{s*}^{w}$, and $\bar{C}_s^{w}$ can be written as

$$\bar{C}_s^{o} = \frac{n_s^{o}}{V_o}, \qquad [II\text{-}12]$$

$$\bar{C}_s^{w} = \frac{n_s^{w}}{V_w}, \qquad [II\text{-}13]$$

and

$$\bar{C}_{s*}^{w} = \frac{n_s^{w} + n_s^{o}}{V_w} \qquad [II\text{-}14]$$

Combining Equations II-11 and 12 gives an expression

$$n_s^{o} = V_o\, k_s^{o/w}\, \bar{C}_s^{w}, \qquad [II\text{-}15]$$

so that combining Equations II-13 through 15 gives an expression for $\bar{C}_{s*}^{w}$ ($\bar{C}_s^{w}$) or

$$\bar{C}_{s*}^{w} = \bar{C}_s^{w}\left[\frac{V_w + k_s^{o/w} V_o}{V_w}\right] \qquad [II\text{-}16]$$

Combining Equations II-10 through II-16 gives the foam area relationship for soil addition (V_o) as

$$\frac{A^{\sigma}}{A_*^{\sigma}} = \left[\frac{V_w}{V_w + V_o k_s^{o/w}}\right]^{\frac{RT}{\bar{E}}} \qquad [II\text{-}17]$$

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