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6 Properties of Surfactant Mixtures

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6.1 Introduction

Many amphiphilic chemicals are very active at various interfaces, and can form aggregates in solution. The characteristic properties of surfactants have been widely applied in many processes, such as flotation, detergency, enhanced oil recovery, paint formulation, lubrication, coating, and deposition. This has been addressed in preceding chapters. Micelles in solution and the aggregates at interfaces also present unique micro environments, which can be utilized for controlling many processes at a level that often cannot be achieved in macroscopic systems. This makes surfactants potentially useful in novel separation and reaction schemes that include magnetic isotopic separation, solar energy conversion, catalysis, and polymer synthesis.

Commercially used surfactants are invariably mixtures of different surface-active compounds. They are usually made from feedstocks that have mixed chain lengths and, depending on their method of synthesis, they are often mixtures of isomers resulting from uncompleted reactions. It is usually not feasible to purify these surfactants to any great extent for obvious economic reasons. On the other hand, isometrically pure surfactants generally may not have any advantage in performance over the less expensive surfactant mixtures. In most applications, well-chosen surfactant mixtures perform significantly better than single components. Mixed surfactants usually exhibit synergism or antagonism under different conditions, and these effects can be used to control the behavior of mixed surfactants for desired formulations and properties. In view of the complexity of practical surfactant formulations, to effectively use the synergistic effects it is helpful to understand interactions among surfactants and the manner in which these interactions affect final product performance.

Most surfactant-related products are complex formulations involving two or more surfactants. The success of a formulation as a consumer product depends on a combination of many factors, including their multifunctional performance profile and aesthetic factors such as product stability, viscosity, and clarity. All of the ingredients in the formulation, especially the surfactants, interact with each other to affect these criteria. Mixed surfactants frequently show synergistic or antagonistic interactions in system. These effects can be manifested as enhanced surface activity, wetting, foaming, detergency, and many other phenomena. In some cases, the interaction among surfactants can also be used to curb undesired behavior such as adsorption in enhanced oil recovery processes.

In this chapter, methods to predict and manipulate the synergism and antagonism of surfactant mixtures is considered along with the relationships of commonly measured surface-activity properties, such as surface tension and critical micellar concentration (*cmc*), to the critical product criteria. Also, the application of surfactant mixtures in a couple of different areas is discussed, with emphasis on properties of surfactant mixtures such as synergism and antagonism. Methods using interaction parameters and Hydrophile-Lipophile Balance (HLB) to characterize the properties of surfactant mixtures are reviewed.

6.2 Applications of Surfactant Mixtures

6.2.1 Surfactants in Agrochemical Formulations

Surfactants have two main applications in agriculture. One application is as formulation aids. They are used as emulsifiers and dispersing agents in emulsifiable concentrates, suspension concentrates, water dispersible granules, and wettable powders. Almost all formulations use surfactant mixtures. The other major application is as activity enhancers, where the use of surfactant along with a herbicide or insecticide can increase the activity of the functional ingredients so that lower quantities of active ingredients are released into the environment.

The successful employment of active agrochemicals depends on correct formulations that can be applied for crop protection, with no harm to those applying the material, to animal life, and to the environment in general. The most important method of application for agrochemical actives is spraying, and here surfactants are employed to produce a variety of "concentrates" in water, oil or powder forms. These concentrates have to be dilutable and maintain sufficient stability upon dilution to be readily applied without problems of separation. All these properties depend on the suitable surfactant composition in the formulation. Typical emulsible concentrate formulations are given below [1]:

1. Bromophos, 2,5-dichlorophenyl O,O-dimethyl phosphorothioate, a nonsystemic contact and stomach insecticide

Bromophos	50% (w/v)
Calcium dodecylbenzensulphonate	2.5%
Castor oil ethoxylate (40 moles EO)	2.5%
Hydrocarbon solvent	to 100 vol.

2. 2.4-D isooctyl ester

2.4-D isooctyl ester	93% (w/v)
Isopropylamine salt of dodecylbenzenesulphonic acid	4.2%
Nonylphenol ethoxylate (EO 8)	2.8%

This is a solvent-free formulation. 2.4-D isooctyl ester is a member of the family of salts and esters of acetic acid. They are all systemic herbicides widely used for weed control in cereals and other crops.

3. Captan

Captan	91% (w/v)
Nonylphenol ethoxylate-formaldehyde condensate	3%
Ammonium salt of nonylphenol ether (EO 4) sulfate	2.5%

Sodium salt of naphthalene sulphonic acid-formaldehyde Condensate	3%
Binder	0.5%

Captan is a fungicide used to control disease in many fruit and vegetable crops. It is also used to protect young plants by sparying. A plant's roots may also be dipped in captan to prevent rot.

In all the examples given above, surfactant mixtures are used. These surfactant mixtures have to be tailored to the active agrochemical in question. A "balanced pair" of surfactants is carefully selected. More information about active agrochemicals can be found in the literature [1–2].

6.2.2 Surfactants in Foam Control

The application where synergism of surfactants is most significant is probably in the area of defoamers. Defoamers are generally used at low concentrations (0.01 to 2%). The correct choice of surfactants can lead to improvements in efficiency of 10 to 100-fold. Such formulations are kept as trade secrets with preparation itself more of an art than a science. In general, the following properties are the most important in choosing the formulations for defoamers:

- lower surface tension than the foaming medium
- insoluble in the foaming medium
- resistant to solubilization and/or degradation by the foaming medium
- positive spreading coefficient to allow spreading on the air–liquid interface.

As a class, silicone defoamers are generally regarded as "universal defoamers." They combine two properties rarely found for the same compound, non-volatility and low surface tension. They are chemically inert and are insoluble in water and many organic solvents. This type of defoamer consists mainly of polydimethylsiloxane with other co-surfactants. Typical defoamer formulations are given below [3]:

1. Defoamer used in textile dyeing

Ingredient	Percent by weight
Anionic surfactant	10–20%
Insoluble or sparing soluble propoxylate	15–35%
Silicone antifoam compound	0.1–2%
Water	40–75%

2. Antifoams for paints

Ingredient	Parts by weight
Paraffin oil	2
Ethylenebis (stearamide)	2.5
Polymethacrylate	3
Silicone surfactant	1.5

The above mixture is heated to 150 °C, and the hot mixture is added to paraffin oil (21 parts by weight) at 25 °C and then cooled to 50 °C. This is then added to the following:

Ingredient	Parts by weight
Paraffin/naphthenic oil	5
Paraffinic oil	6
Hydrophobic silica in oil	8
Castor oil+15EO	1
Water	49
Formaldehyde	0.1

3. Defoamer for domestic dishwashing

Ingredient	% by wt.
Nonionic surfactant antifoam (Polyoxyethylene/Polyoxypropylene)	3
Inorganic salts	95
Bleach (chlorine-releasing agent)	2

In all the formulations of defoamer, careful specification of the surfactant mixtures, the order of addition of components, and rates of heating and cooling are crucial. The detailed information about defoamer formulations can be found in the literature [3].

6.3 Behavior of Surfactant Mixtures

6.3.1 Ideal Mixing of Surfactants

Basically, the formation of micelles of surfactants can be treated as the formation of a new phase, with the micelle as the condensed "phase" in equilibrium with its "vapor," the unassociated monomer. Behavior of surfactant mixtures can be conveniently characterized by introducing the thermodynamic function of mixing, Δm. Denoting a generic molar mixture property by the symbol m, Δm can be defined as the difference between the value of any function in a mixture m and the sum of its values of unmixed components at the same pressure and temperature:

$$\Delta m = m - \sum X_i m_i \ (constant\ T, P) \tag{6.1}$$

where X_i is the molar fraction of surfactant i in mixed micellar phase. Expressions of Δm are particularly simple for ideal mixing systems. The basic results are summarized in Table 6.1. It

Table 6.1 Changes in Properties for Mixing of Ideal Mixtures

$\Delta v^{id} = 0$

$\Delta h^{id} = 0$

$\Delta s^{id} = -R \sum x_i \ln x_i$

$\Delta g^{id} = RT \sum x_i \ln x_i$

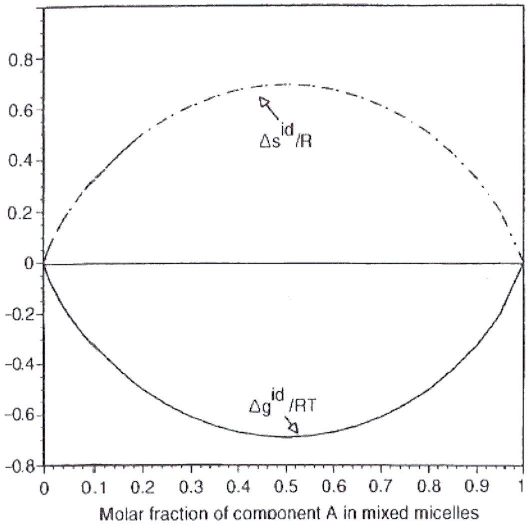

Figure 6.1 The entropy change of mixing and Gibbs energy change of mixing for ideal binary solutions

can be seen that both the volume change of mixing, Δv^{id}, and the enthalpy change of mixing, Δh^{id}, are zero, reflecting the molecular assumptions inherent in the ideal mixing model. However, neither the entropy change of mixing, Δs^{id}, nor the Gibbs energy change of mixing, Δg^{id}, is zero: Δs^{id} is always positive, and Δg^{id} is always negative. For binary systems, the composition dependence of the scaled quantities $\Delta s^{id}/R$ and $\Delta g^{id}/RT$ is shown in Fig. 6.1. Mixtures of surfactants that belong to the same hydrophobic and hydrophilic class, such as a pair of homologous alkyl ethoxylates, may exhibit a behavior very close to ideal mixing. The properties of ideal mixed surfactant systems, such as the *cmc* of mixtures and micellar composition at different concentrations, can be accurately calculated from the *cmc*s of individual components.

6.3.2 Non-ideal Mixing of Surfactants

Almost all surfactant mixtures are non-ideal. One can however, consider the ideal mixture as a basis for the definition of a class of functions m^E, excess properties:

$$m^E = m - m^{id} \text{ (Const. T, P, X)} \tag{6.2}$$

or

$$m^E = \Delta m - \Delta m^{id} \text{ (Const. T, P, X)} \tag{6.3}$$

A common feature of all excess properties is that m^E approaches zero as any component approaches purity:

$$\lim_{x \to 1} m^E = 0 \; (any\ i) \tag{6.4}$$

The excess properties provide global measures of deviations from the ideal mixing behavior. The various excess properties are interrelated. In fact, by choosing T, P, and composition as independent variables, one can view the excess Gibbs energy g^E as a generating function for all the other excess properties. (Eq. 6.3) can then be re-written as:

$$g^E = \Delta g - \Delta g^{id} \text{ (Const. T, P, X)} \tag{6.5}$$

For any mixed surfactant system, if g^E is not zero, the mixing is non-ideal. One of the most popular models for treating such systems is the regular solution theory introduced first by Rubingh [4]. In the case of binary surfactant systems, regular solution theory is based on the assumption that the excess Gibbs free energy of mixture can be given by:

$$\Delta g^E = X_1 X_2 \beta RT \tag{6.6}$$

where X_1 and X_2 are the mole fractions of the two surfactants in the mixed micelle, β the interaction parameter, R the gas constant and T the temperature. The interaction parameter β can be evaluated experimentally from *cmc* measurements and has been widely used to characterize the properties of surfactant mixtures. Mixtures of surfactants which consist of ionic and nonionic surfactants with different hydrophobic or hydrophilic groups usually show some deviation from ideal behavior. An example of a system with non-ideal behavior is shown in Fig. 6.2. The critical micelle concentrations (*cmc*) of the mixture, cationic tetradecyl trimethyl ammonium chloride (TTAC) and nonionic pentadecyl ethoxylated nonyl phenol (NP-15), are plotted in this figure as a function of NP-15 composition. It can be seen that the actual *cmc* is lower than that predicted by ideal mixing, and the mixing between cationic TTAC and nonionic NP-15 is non-ideal. By applying regular solution theory to this system (see next section), an interaction parameter of −1.5 was obtained, and the excess free energy g^E calculated using (Eq. 6.6) for this mixed system is always less than zero. In the case of ionic–nonionic mixtures, the physical origin of the non-ideality lies in the reduction of electrostatic energy as well as complex formation between the surfactants.

6.3.3 Synergism in Surfactant Mixtures

Synergism in surfactant mixtures indicates the fact that these mixtures perform better than the individual surfactant components. An example is an emulsion formation where a mixture of two different surfactants yields a more stable emulsion than would a surfactant with properties intermediate between those of the two surfactants in the mixture. Another example is in the application of detergents. When mixtures of anionic and nonionic surfactants are used to formulate a product, the nonionic surfactant may prevent the calcium sensitive anionic surfactant from precipitating in hard water. The properties of this product are superior to the one containing only the anionic or only the nonionic surfactants.

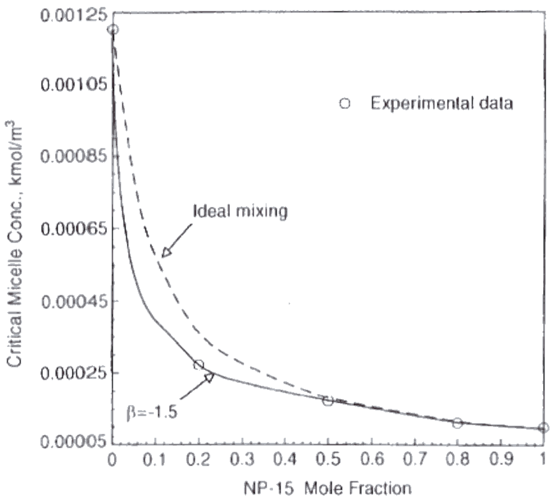

Figure 6.2 Measured *cmc* and theoretical *cmc* calculated from ideal mixing and regular mixing for mixtures of tetradecyl trimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15)

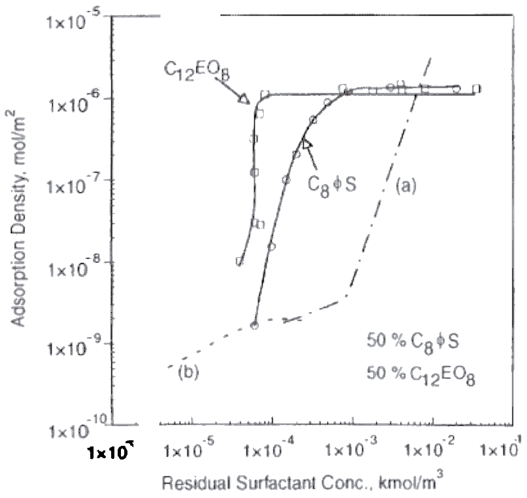

Figure 6.3 Adsorption of C8-benzenesulfonate and $C_{12}EO_8$ alcohol from 50 mol % sulfonate and 50 mol % alcohol mixtures as a function of individual residual surfactant concentration: (a) adsorption of 100% C8-benenesulfonate, (b) adsorption of 100% $C_{12}EO_8$ alcohol; 50 °C; 0.03 M NaCl

Usually, interaction parameter β has been used to elucidate the mixing behavior of binary surfactant systems. When interaction parameter β is negative (see Fig. 6.2), the *cmcs* of surfactant mixtures are lower than predicted by ideal mixing. In this case, the negative deviation from ideality reflects the synergistic effect of the mixture.

Synergism of surfactant mixtures can also be seen in their adsorption. Figure 6.3 shows the isotherms for adsorption of sodium p-octylbenzenesulfonate (C_8PhS) and dodecyloxyheptaethoxyethyl alcohol ($C_{12}EO_8$) on alumina from their 1 : 1 mixtures. It is seen that the ethoxylated alcohol adsorbs to a much greater extent than the sulfonate, even though it exhibited only trace adsorption in the absence of the sulfonate. As a result of synergism, adsorption of the sulfonate is also markedly increased. The adsorption isotherm of C_8PhS is shifted to lowered concentrations by more than an order of magnitude. The presence of the nonionic surfactant between the sulfonate ions in the solloids* should enhance sulfonate adsorption by reducing the lateral electrostatic repulsion between the ionic sulfonate head groups. The effect of synergism is also apparent from a comparison of the slopes of the sulfonate adsorption isotherms in the lower concentration region. Co-adsorption with the nonionic surfactant leads to increase in the slope of the pure sulfonate adsorption from 3.7 to 6.6.

6.3.4 Antagonism in Surfactant Mixtures

Antagonism in surfactant mixtures suggests that some surface active properties are downgraded because of the interaction among surfactants in the mixtures. One example of this antagonistic effect is the micellization behavior of mixed fluorocarbon-hydrocarbon systems. In Fig. 6.4, the *cmc* of mixed fluorocarbon (NF) and hydrocarbon (STS) surfactants is plotted as the function of hydrocarbon (STS) mole fraction [5]. It can be seen that the *cmcs* of this system are higher than predicted by ideal mixing. The interaction parameter calculated using regular solution theory is positive. It has been suggested that two types of co-existing mixed micelles can form in fluorocarbon and hydrocarbon surfactant mixtures. This is mainly because of limited mutual solubility between fluorocarbon and hydrocarbon chains.

The antagonistic effect in surfactant mixtures can be found also in adsorption process. The adsorption isotherms of tetradecyl trimethyl ammonium chloride (TTAC) on alumina in the presence of different amounts of pentadecylethoxylated nonyl phenol (NP-15) are shown in Fig. 6.5. In these experiments the TTAC and NP-15 were pre-mixed and then equilibrated with the alumina for 15 hours at pH 10. It is seen that TTAC solloid formation occurs at lower TTAC concentrations in the presence of the nonionic NP-15 but only at the 4 : 1 and 1 : 1 TTAC:NP-15 ratios. At the 1 : 4 ratio however, no sharp increase in adsorption density corresponding to such aggregation is observed over the entire concentration range studied. In all cases, the plateau adsorption density decreases markedly upon the addition of the nonionic surfactant. This is attributed to the competition of the bulky nonionic NP-15 with TTAC for the adsorption sites under saturated adsorption conditions.

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* Solloid: *Surface Colloid*, is the generic term used for adsorbed aggregates, hemimicelles, admicelles and bilayers etc. on the solids in liquids.

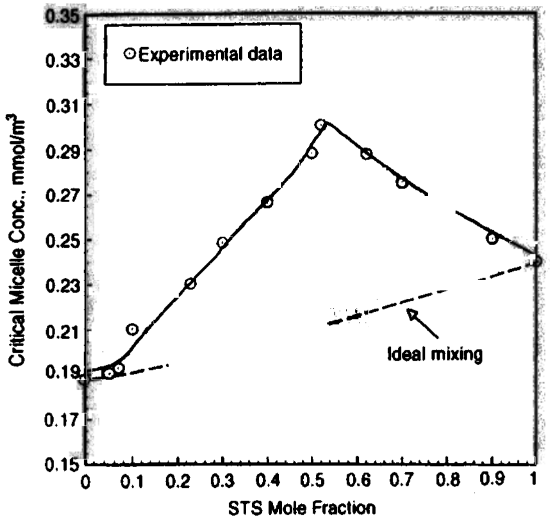

Figure 6.4 Measured *cmc* and theoretical *cmc* calculated from ideal mixing and regular mixing for mixtures of fluorocarbon (NF) and hydrocarbon (STS) (ref. 5)

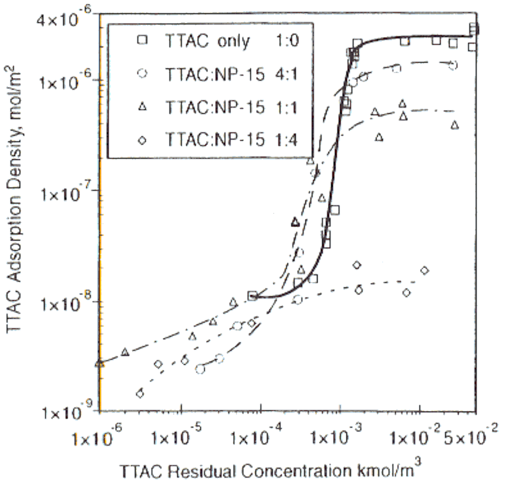

Figure 6.5 Adsorption of tetradecyl trimethyl ammonium chloride (TTAC) in the presence and absence of pentadecylethoxylated nonyl phenol(NP-15), pH 10, 0.03 M NaCl

6.3.5 Solubilization in Mixed Micelles

Above the *cmc*, surfactants in aqueous solutions associate into micro aggregates called "micelles." The hydrophobic part of the surfactant occupies the core of the micelles with the hydrophilic head group pointing toward the bulk water. In this micelle model, the resulting structure resembles a oil droplet surrounded by the polar headgroups.

Aqueous micellar solutions are often used to solubilize solutes. Solutes can interact with micelles hydrophobically in the micelle core, electrostatically with the head group, or by a combination of both mechanisms. The solubility of sparingly water-soluble compounds can be significantly increased by using micellar solution, and surfactant micelles can function as excellent hydrotopes for many solutes in water. For example, 1,2-benzphenanthrene and 2,3-benzphenanthrene have a very low solubility in water ($<9.0 \times 10^{-9}$ M). In the presence of 0.5 M potassium dodecanoate, their solubility increases to about 6.4×10^{-4} M, an increase of 66,000 times.

Aggregates of surfactants can occur also in nonpolar organic solvents. In this case, reverse micelles form with hydrocarbon tails oriented outward into the bulk solvent and hydrophilic headgroups oriented inward. These reversed micelles can be used to solubilize polar solutes in nonpolar solvents.

The term maximum additive concentration (MAC) is often used to denote the solubility of a solute in a given surfactant system, and MAC is defined as the saturated solubilization capacity for a solute expressed as moles of the solubilized solute per mole of micellized surfactant. The additivity mixing rule described by (Eq. 6.7) is used to treat solubilization in mixed micellar systems:

$$S = \sum_i X_i S_i \tag{6.7}$$

where S is solubilization capacity (MAC or other solubilization properties) in mixed micellar system, S_i is solubilization capacity in the pure micellar system of surfactant i, and X_i is mole fraction of surfactant i in mixed micelle. The additivity rule suggests that solubilization capacity in mixed micellar systems varies linearly with surfactant mole fraction in the mixed micelles. There are three cases of observed solubilization capacity in mixed micellar systems: larger, smaller, or equal to the capacity calculated using (Eq. 6.7). The first case represents synergistic solubilization effect in the mixed micelles, while the second and the third cases are antagonistic and ideal solubilization effects respectively. The synergistic solubilization effect is important for purposes of detergency and other applications. One example is shown in Fig. 6.6 [6]. A sharp maximum exists in the MAC versus composition of mixed micelles. The synergistic effect occurs as a result of the interaction of the solute with each of the constituent surfactants, as well as the interaction between constituent surfactants in the mixed micelles.

There is no general rule for predicting synergy in solubilization in mixed surfactant systems. Muto et al. studied the MAC values of yellow OB and azobenzene in mixed micellar systems of non-ionic and anionic surfactants [7]. They assumed the ratio of the observed solubility to the solubility calculated using equation 6.7 to represent the efficiency of solubilization in mixed micelles. The efficiency of solubilization has been found to decrease when non-ionic and anionic surfactants are mixed. The extent of the solubilization efficiency depends on the kinds of mixed micelles formed and solutes involved. Other mixed systems,

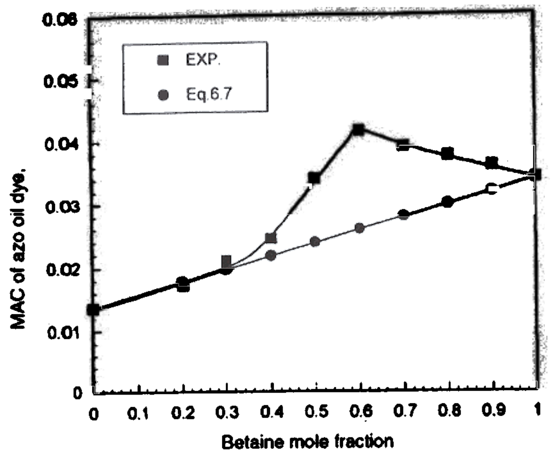

Figure 6.6 Comparison of calculated MAC of azo oil dye with the observed in $C_{12}SO_4Na$/N-tetradecyl-N,N-dimethylbetaine mixed micellar solutions as a function of betaine mole fraction in micelles. Experimental data from (Ref. 6)

for example, oleyl alcohol in aqueous solution of mixed micelles of the lysine-type amphoteric surfactant (DMLL) and $C_{12}SO_4Na$ [8], yields a solubility maximum with respect to the micelle composition, while the DMLL/$C_{16}E_{20}$ system shows a minimum. It is observed that the solubilization behavior in mixed micelles is very complex. For more information on this aspect, readers are referred to the references [6 to 9].

6.3.6 Mixtures Containing Anionic Surfactants

By far the largest class of surfactants in general use are anionic surfactants. Precipitation of surfactants in aqueous solution is a phenomenon of great importance in such applications as detergency and enhanced oil recovery. In general, anionic surfactants are sensitive to multivalent cations in the systems, causing precipitation. By mixing nonionic surfactants with the anionic surfactant products, the salinity tolerance of the surfactants can be markedly improved. The surfactant anion activity is often approximately proportional to the surfactant monomer concentration. At equilibrium, surfactant precipitation occurs if the product of the surfactant anion activity and the counterion activity is above the solubility product of the surfactant salt. Qualitatively, micellization can be considered to be in competition with precipitation for monomers and counterions. The key to increasing salinity tolerance lies in enhancing micelle formation with resultant decrease in monomer concentration. One convenient way to achieve this is by adding nonionic surfactants to anionic surfactant systems. When anionic–nonionic surfactants are mixed, a synergistic effect is usually observed in the micellization of mixtures, and the interaction parameter of surfactant mixtures is negative (about −3 to −5). This is because the nonionic surfactant hydrophilic groups may insert themselves between the hydrophilic groups of the anionic surfactant, decreasing the electrostatic repulsion between the charged anionic groups, and at the same time reducing charge density and the electrical potential at the micelle surface.

There are many papers and patents which report synergistic effects of mixed nonionic surfactants with commonly used anionic surfactants [10, 11]. Nonionic surfactants are generally insensitive to water hardness and very soluble in cold water. Anionic surfactants are effective as detergents for particulate soils but are relatively ineffective for oil. The disadvantages of the anionic surfactants may be overcome by using a mixture with nonionic surfactants. Properly chosen, such a mixture is more surface active than either component alone and possesses the desirable properties of both surfactants.

6.3.7 Mixtures Containing Cationic Surfactants

Cationic surfactants differ from anionic and nonionic surfactants in their high degree of substantivity. The term substantivity encompasses the uptake of surfactant from solution on to a wide variety of negatively charged surfaces: fibers, cellulosics such as paper and cotton, protein, metals, and pigments. Usually cationic surfactants have the ability to kill microorganisms or restrict their growth, and have also been widely used as fabric softeners in the textile industry. When cationic and anionic surfactants are mixed, the interaction between them is very strong, and generally, but not always, they form insoluble complexes. Cationic surfactants can be used in mixtures to reduce interfacial tension and *cmc* and to adjust precipitation boundaries and cloud point behavior by varying the composition of mixtures. For example, $C_{12}E_5$ at 1000 ppm has a cloud point of 32.3 °C; however, addition of 5 ppm C_{16}TAB raises the cloud point to 41.8 °C.

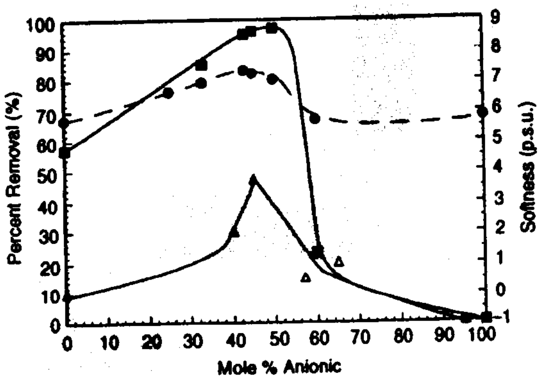

Figure 6.7 Detergency performance and softness benefits of C_{16}TAC-C10 E5SO4Na mixtures as a function of composition. ■ clay soil removal; ● triolein removal; △ softness. The softness was measured relative to a control product by expert graders. A 4 on this scale would indicate a very large difference. (ref. 13)

It has been reported [12] that products which simultaneously provide cleaning and conditioning of human hair, fabrics, or textiles can be formulated by carefully mixing cationic and anionic surfactants. The cationic surfactant composition comprises a mixture of the diethyl sulfate salts of the cyanoethylated fatty acid amides. The anionic surfactants can include such compounds as lauryl sulfates, lauryl ether sulfates, or alkyl benzene sulfonates.

Detergents containing cationic surfactants can provide fabric care benefits such as static control and softness not available with conventional detergents, but cationic surfactant itself does not provide good soil removal. By mixing cationic surfactants with other types of surfactants, synergistic effects can be obtained and multi-functional products can thus be developed. A typical detergency and softness profile is shown in Fig. 6.7 as a function of the cationic/anionic ratio [13]. It can be seen that maximum soil removal and softness effects can be achieved by adjusting the relative ratio of surfactants in the mixtures.

6.3.8 Mixtures of Fluorocarbon and Hydrocarbon Surfactants

As a class, fluorocarbon compounds in which all carbon-hydrogen bonds have been replaced by carbon-fluorine bonds possess very low surface tension and surface energy. Most fluorocarbon surfactants are efficient in reducing the surface tension to levels that cannot be reached with other types of surfactants. Some of these fluorocarbon surfactants are stable and effective in extremely hostile environments, including strongly acidic, alkaline, or even oxidizing systems. In many cases, a combination of fluorocarbon and hydrocarbon surfactants can produce a degree of wetting which cannot be accomplished by either type alone.

Mixed fluorocarbon-hydrocarbon surfactants generally exhibit micellization with positive deviation from ideal mixing (see Fig. 6.4). Co-existence of two types of mixed micelles has been reported in these systems mainly resulting from mutual solubility within their mixed micelles. A schematic phase diagram of micellization is shown in Fig. 6.8. In region I, the surfactant concentration is low, and there are no micelles formed. With the increase in total concentration, (as shown by dashed line), A-rich micelle first forms in region II. Concentration corresponding to curve 1 is called first *cmc* of A-B mixtures. With further increase in total concentration to curve 2, a second type of mixed micelle (B-rich micelle) begins for form (Region III). This mainly results from the limited solubility of component B in A-rich micelle. Concentration corresponding to that of curve 2 is called the second *cmc* of A-B mixtures. When the concentration is further increased to curve 3, the A-rich micelle may disappear. This leads logically to the concept of a critical demicellization concentration or *cdc* (curve 3). In region IV, only B-rich micelle exists.

As mentioned above, these micellization behaviors are attributed to the limited solubility of surfactant B in A-rich micelle. When the mixture is rich with respect to surfactant B, second *cmc* and demixing may not occur. We have also reported that the co-existence of two types of mixed micelles can be found in some hydrocarbon–hydrocarbon mixtures [14]. Understanding the micellization behavior of this type of surfactant mixture is important because many applications of surfactants are directly related to the properties of their micelles in the system.

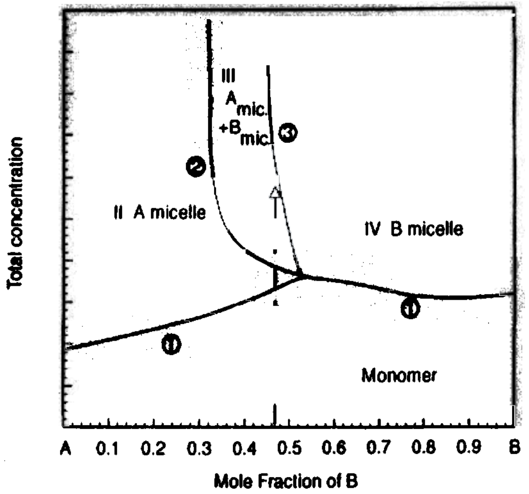

Figure 6.8 Schematic micellization diagram for surfactant mixture A and B where two types of co-existing micelles may form. Region I: No micelle; Region II: A-rich micelle; Region III: Two types of co-existing micelles; Region IV: B-rich micelle

6.4 Characterization of Surfactant Mixtures

6.4.1 Pseudo-phase Separation Approach for Treating Non-ideal Mixed Micellization

In the early 1950s, models for treating mixed micellization in binary surfactant systems were developed based on the pseudo-phase separation approach [15]. Here, micellization is approximated as a phase separation process with the micelle aggregation number taken to approach infinity. Calculations using a monodisperse mass action model show that the pseudo-phase separation model can yield reasonable values for micellar sizes on the order of 50 molecules or more.

A general model can be developed for non-ideal mixed micellization processes by considering the chemical potentials of the individual surfactant components. For mixed surfactant component i in solution, μ_i, the chemical potential of species is given by:

$$\mu_i = \mu_i^0 + RT \ln C_i^m \tag{6.8}$$

where μ_i^0 is standard chemical potential, and C_i^m is monomer concentration of component i.

For the pure micelle of ith component:

$$\mu_i^{0M} = \mu_i^0 + RT \ln C_i \tag{6.9}$$

where C_i is the CMC of pure component i.

For mixed micelle:

$$\mu_i^M = \mu_i^{0M} + RT \ln \gamma_i X_i \tag{6.10}$$

where X_i is the mole fraction of surfactant i in mixed micelles, γ_i is activity coefficient of i in mixed micelles, and OM refers to the pure micelle phase. Under equilibrium conditions:

$$\mu_i^M = \mu_i \tag{6.11}$$

Eq. (6.8) to (6.10) can be combined to yield the following general relationship:

$$C_i^m = \gamma_i X_i C_i \tag{6.12}$$

At the mixed *cmc*, Eq. (6.12) becomes:

$$\alpha_i C^* = \gamma_i X_i C_i \tag{6.13}$$

where C^* is the mixed *cmc* and α_i is the mole fraction of surfactant i in the mixed solution. With the constraint:

$$\sum_{i=1}^{n} X_i = 1, \tag{6.14}$$

Eq. (6.13) and (6.14) can be combined to yield the following:

$$\frac{1}{C^*} = \sum_{i=1}^{n} \frac{\alpha_i}{\gamma_i C_i} \tag{6.15}$$

By re-arranging the above equations, the following expressions for monomer concentrations and mixed micellar composition in a binary surfactant system can be obtained:

$$X_1 = \left| \frac{-(C-\Delta) + [(C-\Delta)^2 + 4\alpha C\Delta]^{1/2}}{2\Delta} \right| \tag{6.16}$$

$$\left[\frac{-(C-\Delta) + [(C-\Delta)^2 + 4\alpha C\Delta]^{1/2}}{2 \cdot (\gamma_2 C_2/\gamma_1 C_1 - 1)} \right] \tag{6.17}$$

$$C_2^m = \left[1 - \frac{C_1^m}{\gamma_1 C_1} \right] \cdot \gamma_2 C_2 \tag{6.18}$$

$$(\Delta = \gamma_2 C_2 - \gamma_1 C_1)$$

where X_1 is the mole fraction of surfactant 1 in mixed micelles, $\gamma_i (i = 1, 2)$ is the activity coefficient of i in mixed micelles, C is the total concentration of the surfactant in the mixture, and α is the overall mixing ratio of surfactant 1 in the binary mixture.

Calculations using the above equations are relatively simple. The key point of this kind of treatment involving a phase segregation model lies in the way the activity coefficient γ_i is calculated. In ideal mixing model, γ_i is equal to 1, and the mixed *cmc* and the monomer concentrations of surfactants can be easily calculated. But very few surfactant mixtures fit the ideal mixing model. To handle these non-ideal mixtures properly, suitable models for γ_i must be developed. As mentioned before, regular solution theory has been widely used to model interactions in mixed surfactant systems. In the case of binary surfactant systems, based on the Eq. (6.6), the activity coefficients γ_i for binary mixtures can be expressed by the following equations:

$$\gamma_1 = \exp[\beta \cdot (1 - X_1)^2] \tag{6.19}$$

$$\gamma_2 = \exp[\beta \cdot X_1^2] \tag{6.20}$$

The interaction parameter β can be evaluated experimentally from *cmc* measurements and used to interpret other properties in the system. If C_1 and C_2 are the *cmc* values of the pure surfactants and C^* that of the mixed system, the following relationship permit estimation of β in terms of C_1, C_2 and C^*:

$$\frac{X_1^2 \ln\left(\frac{C^*\alpha}{C_1 X_1}\right)}{(1 - X_1)^2 \ln\left[\frac{C^*(1-\alpha)}{C_2(1 - X_1)}\right]} = 1 \tag{6.21}$$

$$\beta = \frac{\ln\left(\frac{C^*\alpha}{C_1 X_2}\right)}{(1 - X_1)^2} \tag{6.22}$$

where X_1 is the mole fraction of surfactant 1 in the mixed micelle and α is the mole fraction of surfactant 1 in the total mixed solute. (Eq. 6.21) must be solved iteratively for X_1, and substitution of this X_1 into (Eq. 6.22) results in a solution for β. Here β is a measure of the deviation of the mixture behavior from ideality.

The regular solution treatment is useful because of its simplicity and easy application to mixing phenomena. But it should be mentioined that the basic assumption in this treatment, i.e., mixing entropy is zero, is not thermodynamically valid for describing non-ideal mixed micelles. Therefore, this model should be viewed as a useful empirical model. During the last two decades, regular solution theory has been applied to a number of binary surfactant systems and the interaction parameter β for many surfactant mixtures has been evaluated. These data are very important for understanding the strength of interaction between surfactants. Since the interaction parameter is related to excess free energy (see Eq. 6.6), a negative value indicates an attraction between surfactants, or synergism in the micellization processes; a positive value, in contrast, indicates repulsion between surfactants, or antagonism in the micellization processes. The bigger the interaction parameter β, the stronger the attractive or repulsive interaction. When the β is close to zero, the mixed system approaches ideal mixing. Some available interaction parameters are summarized in Table 6.2. A knowledge of the interaction parameter for mixed binary surfactant systems allows prediction of the *cmc* of mixtures from the *cmcs* of pure components. The monomer concentrations and the composition of mixed micelles can also be calculated using the above equations. These are the most important parameters which determine the behavior of surfactant mixtures in different applications.

Table 6.2 Interaction Parameters for Some Binary Surfactant Mixtures

Mixtures	Type	Medium	T (°C)	β
$C_{12}SO_4Na/C_{12}E_8$		H_2O		−3.9
$C_{12}SO_4Na/C_{12}E_8$		0.5 M NaCl		−3.0
$C_{12}SO_4Na/C_{10}E_4$		0.5 mM Na_2CO_3		−3.6
$C_{12}SO_4Na/C_8E_{12}$		H_2O		−4.1
$C_{12}SO_4Na/C_8E_6$		H_2O		−3.4
$C_{12}SO_4Na/C_8E_4$		H_2O		−3.1
$C_{12}E_2SO_4Na/C_8E_4$		H_2O		−1.6
$C_{12}E_2SO_4Na/C_{12}E_{10}$		0.1 M NaCl		−2.3
$C_{15}SO_4Na/C_{10}E_6$		H_2O		−4.3
$C_{12}SO_4Na/C_{16}E_{10}$		H_2O		−6.6
$C_{12}SO_4Na/C_{16}E_{20}$		H_2O		−6.2
$C_{12}SO_4Na/C_{16}E_{30}$		H_2O		−4.3
$C_{12}SO_3Na/C_{12}E_8$		H_2O		−3.4
$C_{12}SO_3Na/C_{12}E_7$		H_2O		−2.4
$C_{12}SO_4Na/NPE_{10}$		0.03 M NaCl		−3.0
$C_{12}SO_4Na/NPE_{10}$		0.4 M NaCl		−1.6
$C_{12}\Phi SO_3Na/NPE_{10}$		0.17 M NaCl		−1.5
$C_{12}SO_4Na/NPE_{15}$		H_2O		−5.4
$C_{12}\Phi SO_3Na/NPE_{10}$		0.15 M NaCl		−3.2
$C_{12}\Phi SO_3Na/NPE_{10}$		0.15 M NaCl		−2.8
$C_{12}\Phi SO_3Na/NPE_{10}$		0.15 M NaCl		−2.1
$C_{12}\Phi SO_3Na/NPE_{10}$		0.15 M NaCl		−1.8
AOT-$Na/C_{12}E_5$		H_2O		−1.2
AOT-$Na/C_{12}E_7$		H_2O		−1.9
AOT-$Na/C_{12}E_8$		H_2O		−2.0
AOT-$Na/C_{12}E_8$		0.05 M NaCl		−3.6
LAS-$Na/C_{12}E_{10}$		0.1 M NaCl		−2.7
$C_{12}SO_4Na/C_{10}PO$		1 mM Na_2CO_3		−3.7
$C_{12}SO_4Na/C_{10}MSO$		1 mM Na_2CO_3		−2.4
$C_{10}TABr/C_8E_4$		0.05 NaBr		−1.8
$C_{12}TACl/C_{12}E_5$		H_2O		−1.0
$C_{14}TABr/C_{10}E_5$		H_2O		−1.5
$C_{16}TACl/C_{12}E_5$		H_2O		−2.4
$C_{16}TABr/C_{12}E_5$		H_2O		−3.0
$C_{16}TACl/C_{12}E_8$		0.1 M NaCl		−3.1
$C_{18}TACl/C_{12}E_5$		2.4 mM NaCl		−2.6
$C_{20}TACl/C_{12}E_8$		H_2O		−4.6
$C_{12}PyrCl/C_{12}E_8$		H_2O		−2.7
$C_{12}PyrCl/C_{12}E_8$		0.1 M NaCl		−1.4
$C_{12}PyrCl/C_{12}E_8$		0.5 M NaCl		−1.0
$C_{12}PyrCl/NPE_{10}$		0.03 M NaCl		−1.3
$C_{14}TACl/NPE_{15}$		0.03 M NaCl		−1.5
$C_{16}TACl/NPE_{10}$		0.03 M NaCl		−1.7
$(C_{12})_2Me_2NBr/C_{12}E_5$		H_2O		−1.6
C_8SO_4Na/C_8TABr		H_2O		−10.5
$C_{10}SO_4Na/C_{10}TABr$		H_2O		−18.5
$C_{10}SO_4Na/C_{10}TABr$		0.05 M NaBr		−13.2
$C_{12}SO_4Na/C_{12}TABr$		H_2O		−25.5
$C_{12}SO_4Na/C_{12}TABr$		H_2O		−25.5
C_{16}-2-Φ-$SO_3Na/C_{14}TABr$		H_2O		−19.4
C_{16}-4-Φ-$SO_3Na/C_{14}TABr$		H_2O		−17.2
C_{16}-6-Φ-$SO_3Na/C_{14}TABr$		H_2O		−16.1
C_{16}-8-Φ-$SO_3Na/C_{14}TABr$		H_2O		−15.3
C_{14}-7-Φ-$SO_3Na/C_{14}TABr$		H_2O		−17.3
C_{12}-6-Φ-$SO_3Na/C_{14}TABr$		H_2O		−18.7
C_{10}-5-Φ-$SO_3Na/C_{14}TABr$		H_2O		−19.9
$C_{12}SO_3Na/C_{14}TABr$		H_2O		−20.0
$C_{12}SO_4K/C_{12}NMeO$		H_2O		−16.5
$C_{12}Np/C_{12}SO_4Na$		H_2O		−14.1
$C_{12}Np/C_{14}SO_4Na$		H_2O		−15.5
$C_{12}BMG/C_{12}SO_4Na$		H_2O		−5.0
$C_{12}BMG/C_{12}TABr$		H_2O		−1.2
$C_{12}BMG/C_{12}E_8$		H_2O		−0.9
$C_{12}N(Me)_2O/C_{12}SO_4Na$		0.5 mM $NaCO_3$		−4.4
$C_{12}S(Me)O/C_{12}SO_4Na$		1 mM $NaCO_3$		−2.4
$C_{10}P(Me)_2O/C_{12}SO_4Na$		1 mM $NaCO_3$		−3.7
$C_{12}N(B_z)(Me)CH_2COOH/C_{12}SO_3Na$		pH 5.0		−5.4
$C_{12}N(B_z)(Me)CH_2COOH/C_{12}SO_3Na$		pH 5.8		−5.0
$C_{12}N(B_z)(Me)CH_2COOH/C_{12}SO_3Na$		pH 6.7		−4.4
$C_{12}N(Me)_2CH_2COOH/LASNa$		0.1 M NaCl, pH 5.8		−2.9
$C_{12}N(Me)_2CH_2COOH/LASNa$		0.1 M NaCl, pH 9.3		−1.7
$C_{10}PO/C_{10}MSO$		1 mM $NaCO_3$		0.0
$C_{10}E_3/C_{10}MSO$		H_2O		−0.1
$C_{12}E_3/C_{12}E_8$		H_2O		−0.4
$C_{12}AO/C_{10}E_8$		0.5 mM $NaCO_3$		−0.8
$C_{16}TACl/C_{12}PyrCl$		0.15 NaCl		−0.2

Abbreviations A = Anionic; C = Cationic; Z = Zwitterionic; N = Nonionic; Pyr = $-(CH_3)-NC_5H_5$ NP = Nonyl phenol; $C_{12}BMG = C_6H_5-CH_2-C_{12}-N-CH_3-CH_2-COO^-$; $E = (-CH_2CH_2O-)$; AOT = di(2-ethylhexyl) sulfosuccinate; $B_z = C_6H_5CH_2-$; LAS = C_{12} benzensulfonate; Me = CH_3-; $\Phi = -C_6H_4-$; Np = $-NH_2-CH_2-CH_2-COO^-$; TA = Trimethyl Ammonium; MSO = Methyl sulfoxide; PO = dimethyl phosphine oxide

6.4.2 Hydrophile-Lipophile Balance of Mixed Surfactants

The term Hydrophile-Lipophile Balance (HLB) was first suggested by Clayton, referring to the balance between the hydrophilic and lipophilic parts of a surfactant molecule. Griffin later developed the concept of HLB for emulsifiers on the basis of their aqueous solubility. The HLB value is an experimental number initially assigned to nonionic surfactants on the basis of a wide variety of emulsion tests, but his concept is not limited to just this group of surfactants. It can also be applied to anionic and cationic surfactants. Extensive literature exists on HLB of surfactants [16], which is useful for selecting surfactants and their mixtures for required applications. HLB ranges for various applications are shown in Table 6.3 [17]. Methods to estimate HLB values of surfactants, especially their mixtures, is discussed next. These methods are good not only for evaluating the HLB number, but also offer a convenient way to analyze the behavior of surfactants and their mixtures.

It has been found that the HLB values of mixtures of two or more surfactants are additive: the HLB value of the mixture is equal to the sum of the HLB values of the constituents multiplied by their weight fraction in the mixtures X_i^w:

$$\mathrm{HLB} = \sum_i X_i^w (\mathrm{HLB})_i \tag{6.23}$$

For example, a blend of four parts of sorbitan monolaurate (HLB = 8.6) and six parts of alkyl aryl sulfonate (HLB = 11.7) has an effective HLB of $0.4 \times 8.6 + 0.6 \times 11.7 = 10.46$.

For most polyhydric alcohol fatty acid esters, approximate HLB values may be obtained using the following equation:

$$\mathrm{HLB} = 20(1 - \mathrm{S}/\mathrm{A}) \tag{6.24}$$

where S is the saponification number of the ester and A is the acid number of the acid. Thus, for a glycerol monostearate with S = 161 and A = 198, an HLB number of 3.74 can be obtained using (Eq. 6.24). Accordingly, this surfactant would be considered to be of low hydrophilicity.

Many fatty acid esters do not give reliable saponification data. For these substances, the HLB values may be calculated by:

$$\mathrm{HLB} = (\mathrm{E} + \mathrm{P})/5 \tag{6.25}$$

where E is the weight percent of oxyethylene and P is the weight percent of polyhydric alcohol. It should be emphasized that Eq. (6.24) and (6.25) are not applicable to surfactants containing polyoxypropylene or polyoxybutylene groups or to ionic surfactants. To calculate these HLB numbers, Davies devised a method that assigns an HLB group number to each functional group in a molecule based on the relative coalescence rate of oil droplets in water and water droplets in oil. These numbers are summarized in Table 6.4 [18]. By using these numbers, HLB of surfactants or their mixtures can be calculated as:

Table 6.3 HLB Ranges and Suitable Applications [17]

HLB Range	Applications
HLB by Dispersibility	
1 to 4	No dispersibility in water
3 to 6	Poor dispersion
6 to 8	Milky dispersion after vigorous agitation
8 to 10	Stable milky dispersion
10 to 13	Translucent to clear dispersion
>13	Clear solution

Table 6.4 HLB Group Number [18]

Hydrophilic	Group Number	Hydrophobic	Group Number

$$\mathrm{HLB} = \sum (\text{Hydrophilic group number}) - \sum (\text{Hydrophobic group number}) + 7 \tag{6.26}$$

This method is useful if the structure and proportions of the components in surfactants are known. However, (Eq. 6.26) contains the implicit assumption that all ethylene oxide groups make the same hydrophilic contribution, and the contribution of a given hydrophilic group to the polarity of a surfactant molecule tends to decrease as the size of the molecule increases. This assumption cannot be considered to be strictly correct.

By using interaction parameters and HLB data, the behavior of surfactant mixtures can be characterized well, but it should also be noted that all these methods are based on some assumptions. Not all properties of surfactant mixtures can be predicted by these methods. More fundamental work is needed to fully understand the behavior of surfactant mixtures. However, it is clear that synergism or antagonism among surfactants is present in most surfactant mixtures used for various applications. The behavior of surfactant mixtures can be thus manipulated by controlling these effects so that desired performance can be obtained.

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Appendix I

Suppliers Mentioned in the Text

Air Products	7201 Hamilton Blvd., Allentown, PA 18195 215 481 4911
Akzo-Nobel,	Velperweg 76, 6824BM, Arnhem, Netherlands US: 312 906 7500
Albright and Wilson	US: PO Box 26229, Richmond, VA 23260 804 550 4300
Amoco	204 E. Randolf Dr., Chicago IL, 60601 312 856 5111
Arco Chemicals	3801 Westchester Pike, Newtown Square, PA 19073 215 359 2000
Arizona Chemical	101 E.Hway 98 Panama City, FL 32401 904 785 6700
BASF	3000 Continental Dr., N., Mount Olive, NJ 07828 201 316 3000
Bayer	One Mellon Ctr., 500 Grant St. Pittsburgh, PA 15219 412 394 5500
Chemithon	5430 Marginal Way SW, Seattle, WA 98106 206 937 9954
Chevron	PO Box 3766 1301 McKinney, Houston TX 77253 713 754 4161
Colgate Palmolive	300 Park Ave., New York, NY 10022 212 310 2000
Condea-Vista	900 Threadneedle St., Houston TX, 77079 713 588 3000
Croda	7 Century Dr., Parsipanny, NJ 07054 201 644 4900
Crompton and Knowles	1595 MacArthur Blvd., Mahwah, NJ 07430 201 818 1200
Cytec	1105 N. Market St., Wilmington, DE 19801 203 321 2521
Dow Brands	PO Box 68511 Indianapolis, IN 46268 800 447 4369