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Solubilization of sodium cocoyl isethionate

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Synopsis

Sodium cocoyl isethionate (SCI) has been a predominant ingredient in syndet bar formulation for more than thirty years. Although cost effective and well recognized for good skin compatibility, SCI is not regularly found in liquid detergent systems due to its limited solubility in water. This study focuses on the understanding of enthalpy of solubilization, equilibrium of solubilization, and the structures and properties of sodium cocoyl isethionate and various surfactants. The purpose of this exercise is to help the formulator to find appropriate surfactant systems to keep sodium cocoyl isethionate in aqueous solution.

The solubility of SCI in water is unfavorable in terms of enthalpy of solvation. When setting up equilibrium of solubilization, there are three possible phases, and three methods have been developed to prevent SCI from recrystallizing in aqueous solutions. The first focuses on tying CI^- ions within micelles made of secondary surfactants. The second focuses on the exchange of sodium ions with ammonium ions (and/or triethanolamonium). The third centers on emulsification of SCI and the subsequent change of micelles into emulsified oil drops. A combination of two or three of these methods will enable the formulator to use SCI as the primary surfactant in liquid detersive systems.

INTRODUCTION

Owing to its excellent skin compatibility, mildness, and emollient properties, sodium cocoyl isethionate (SCI) has been used extensively in syndet bars (1–6). SCI has become cost efficient because of its broad application in personal care. Chemists try to incorporate SCI within liquid detersive systems in order to take advantage of both its excellent performance characteristics and its cost efficiency. However, SCI is not widely used in liquid cleansing systems because of its limited solubility in water.

Some proprietary technologies have been developed to increase the aqueous solubility of SCI (7–9). Zwitterionic detergents (betaines) were discovered to increase the solubility of SCI in liquid detersive compositions (7). In such systems, SCI, betaine(s), and other anionic surfactants (other than SCI) are the three major surfactants. Alkylamphoacetates are another category of surfactants disclosed to increase the solubility of SCI (8). N-methyl cocoyl taurate and laureth sulfate are also used as major surfactants in these proprietary technologies. Nonionic sugar surfactants selected from the group consisting of alkyl glucose esters, aldobionamides, gluconamides, glyceramides, glyceroglycolipids, polyhydroxy fatty acid amides, and alkyl polyglycosides can also increase the solubility of SCI (9). Selected sugar surfactants, SCI, and free fatty acid are the three major ingredients in most proprietary compositions.

These proprietary technologies do not explain why some ingredients dissolve SCI in terms of fundamental physical principles. This article will try to bridge the gap in this understanding by focusing on the enthalpy of solubilization, the equilibrium of solubilization, and the structures and properties of SCI and various surfactants.

MATERIALS

The trade names of materials used in this study are as follows: sodium cocoyl isethionate (85% active): Hostapon SCI 85® (Clariant GmbH) and Jordapon Cl Prill® (BASF); ammonium cocoyl isethionate (25% active): Jordapon ACI-30 G® (BASF); emulsifying wax NF: Polawax® (Croda); disodium laureth sulfosuccinate: Mackanate EL® (Mcintyre); polysorbate 20 and polysorbate 80: Tween-20® and Tween-80® (Uniqema). There are many other common surfactants from the Mcintyre Group Ltd, Chemron Corporation, and the Stepan Company.

PRINCIPLES

Enthalpy of solvation will be used to understand why ammonium cocoyl isethionate (ACI) is more soluble than SCI. Hess's law states that the enthalpy of a reaction is the same whether the reaction takes place in one or several steps (conservation of energy). Born and Haber (10) applied Hess's law to the enthalpy of solubilization of ionic compounds in water (Figure 1). The overall enthalpy of the solubilization process is the sum of two terms: the enthalpy of ion dissociation from the lattice matrix (lattice energy) and the enthalpy of introducing the dissociated ions into the solvent (solvation energy). $\Delta H_{\text{solubilization}} = U + \Delta H_{\text{solvation}}$.

Size and other characteristics of ions are two main factors in determining lattice energy and solvation energy. Statistical calculation and experimental analysis show that the enthalpy of solvation is of roughly the same order of magnitude as the enthalpy of lattice energy. Thus the total change of enthalpy of solubilization can be either positive, negative, or zero, depending upon the particular compound. In cases where the enthalpy

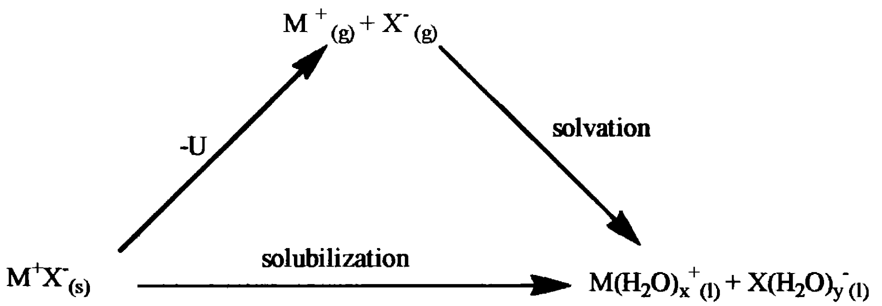


Figure 1. Born-Haber cycle of solubilization of ionic compounds.

is negative, zero, or slightly positive, solubilization will take place. If the enthalpy change is too positive, solubilization will not occur. This is to say that ions within the lattice structure will enter solution if the interactions between solute and solvent are strong enough to overcome the lattice energy.

The enthalpy of solubilization of SCI is slightly positive in terms of the Born-Haber cycle at room temperature. In another words, the lattice energy of SCI is slightly larger than the combined solvation enthalpy of sodium ion (Na^+) and cocoyl isethionate ion (CI^-). Sodium cocoyl isethionate has a solubility of about 0.01% by weight at 25°C in water. Alternatively, ammonium cocoyl isethionate (ACI) is very soluble in water at 25°C. A liquid surfactant in the market has 25% active ACI (by weight). However a 25% active liquid solution of ACI is more costly than an 85% active solid of SCI. Thus a substantial use of ACI within shampoos or liquid cleansing formulas would be limited to more expensive "high-end" products.

SCI and ACI differ chemically only in their cationic ions, Na^+ and $NH_4{}^+$, respectively. Here we focus on the size and characteristics of these cationic ions. Since the ammonium ion is larger in size and has a smaller solvation enthalpy than the sodium ion, -240.1 kJ mol^{-1} for the sodium ion and -132.51 kJ mol^{-1} for the ammonium ion (11), ACI is determined to have smaller lattice energy than SCI because the enthalpy of solubilization of ACI should be negative or slightly negative. Smaller lattice energy means that the energy necessary to solvate ACI should be relatively low in comparison to that of SCI. This will become an important point in the discussion of method II. Unfortunately the lattice energy of ACI and SCI, and the solvation enthalpy of CI^- ion, are not available in the chemical literature for theoretical calculation.

Chemists can find ways to prevent SCI from recrystallizing in aqueous solution at 25°C and below. The following discussion will focus on reaction equilibrium as a means of understanding how to make SCI more soluble in water.

When SCI is dissolved in water, the equilibrium reaction is as follows:

$$NaCI_{(s)} \rightleftharpoons Na^+_{(l)} + CI^-_{(l)} \rightleftharpoons Na^+_{(l)} + MIC(CI^-)_{(l)}$$

Le Chatlier's theorem states that if a system in equilibrium is disturbed, it acts to minimize the disturbance. Any change will make the reaction shift to either the right or left in order to reestablish equilibrium. The phase separation model (6) tells us that micelles constitute a new phase, formed in the system at and above the critical micelle concentration. The equilibrium reaction indicates that it is reasonable to assume there are three possible phases involved in the equilibrium: recrystallizing solid (SCI), monomeric surfactant ions (Na^+ and CI^-), and micelles (MIC) of pure CI^-. Decreasing the concentration of CI^-, Na^+, or MIC(CI) will shift the reaction equilibrium to the right, which leads to a reduction of solid SCI; the solubility of SCI is increased. Increasing the concentration would shift the equilibrium to the left and decrease the solubility of SCI.

Krafft temperature is often used to describe the temperature-dependent solubility of surfactants in water. Surfactant solubility will undergo a sharp, discontinuous increase at some characteristic temperature referred to as the Krafft temperature, T_K. At temperatures below T_K, solubility is determined by the crystal lattice energy (U) and the enthalpy change of hydration of the system $\Delta H_{solvation}$, as stated in the Born-Haber cycle. At temperatures above T_K, the solubility of the surfactant monomer may increase to the point at which micelle formation begins and aggregate forms become thermodynamically stable. In the cases of SCI and ACI, it is apparent that ACI has a lower T_K (below room temperature), since ACI has a very small lattice energy and SCI has a higher T_K (close to the boiling temperature of water) due to its large lattice energy.

METHODS

Three methods of preventing recrystallization of SCI have been developed based on the enthalpy of solubilization and equilibrium. The first focuses on secondary surfactants, which tie up CI^- ions within micelles. The second focuses on the exchange of sodium ions with ammonium ions (and/or triethanolamonium). The third centers on introducing emulsifiers and emollients to change micelles into stable emulsified oil drops.

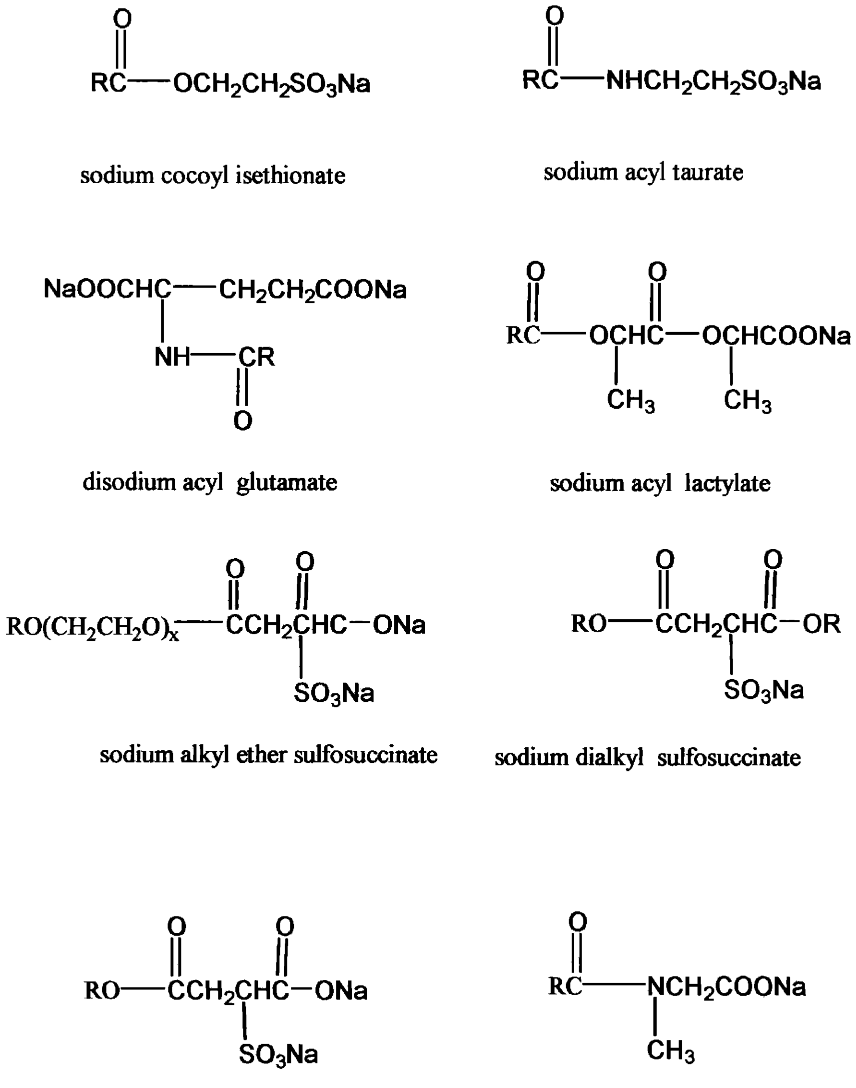
METHOD I: SELECTED SECONDARY SURFACTANTS

When thinking about SCI solvation, it is important to refer to the equilibrium equation stated above. If one modifies an SCI/water system in such a way as to shift equilibrium to the right, away from solid SCI, then its solubility in water is increased. Modifying pure MIC(CI) with specific secondary surfactants will accomplish this goal both by increasing micelle stability and by increasing the number of aqueous CI^- ions that are taken up within micelles.

Generally, there are four types of interactions (or molecular interactions) involved in micelle formation (6). They are: (i) hydrophilic/hydrophobic interaction between surfactant and water molecules; (ii) interaction among solvated head groups (generally repulsive) and between the head groups and co-ions; (iii) attractive interaction among hydrocarbon tails in separate molecules; and (iv) geometric packing constraints derived from the particular molecular structure involved. The last two interactions are very important to the discussion of method I since interactive forces can vary significantly, depending on the surfactants. The second interaction listed will become a focus in method II. In order to tie CI^- ions in micelles without recrystallization, one has to choose surfactants that strongly interact with CI^- ions.

To promote strong interaction with CI^- ions, surfactants should have either similar hydrophilic head groups or larger and complicated hydrophilic head groups. The structure of SCI is depicted in Figure 2 along with the structures of other selected surfactants. Anionic surfactants, amphoteric surfactants, and non-ionic surfactants can serve this purpose. In the anionic surfactant category, these are (but not limited to): sodium (or ammonium) dialkyl sulfosuccinates, disodium (or diammonium) alkyl sulfosuccinates, disodium (or diammonium) alkyl ether sulfosuccinates, disodium (or diammonium) alkylamido MEA sulfosuccinates, disodium (or diammonium) alkylamido MIPA sulfosuccinates, disodium (or diammonium) alkylamido PEG-2 sulfosuccinates, sodium (or ammonium) acyl taurates, disodium (or diammonium) acyl glutamates, sodium (or ammonium) acyl lactylates, and sodium acyl sarcosinate.

In the amphoteric category (Figure 3) there are alkylamidopropyl hydroxysultaines, sodium (or ammonium) alkylamphoacetates, disodium (or diammonium) alkylamphodiacetates, sodium (or ammonium) alkylamphopropionates, disodium (or diammonium) alkyliminodipropionates, alkylamidopropyl betaines, alkylamidopropylamine oxides, and sodium alkylamphohydroxypropylsulfonate.



sodium cocoyl isethionate

sodium acyl taurate

disodium acyl glutamate

sodium acyl lactylate

sodium alkyl ether sulfosuccinate

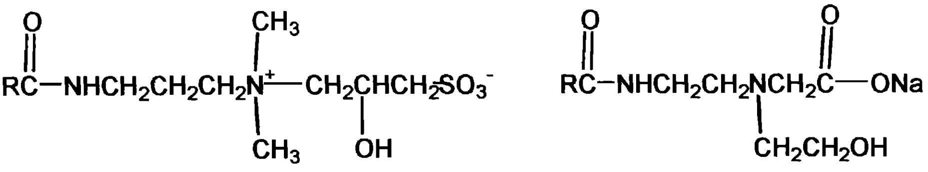
sodium dialkyl sulfosuccinate

disodium alkyl sulfosuccinate

sodium acyl sarcosinate

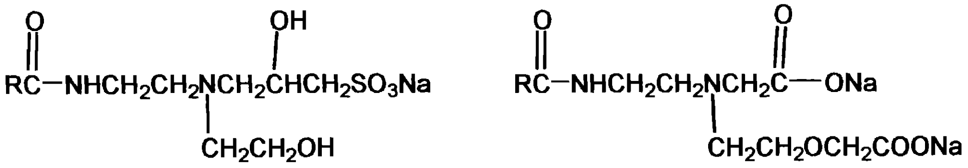
Figure 2. Structures of selected anionic surfactants.

Non-ionic surfactants require complicated and long-chain polyethylene groups to prevent recrystallization of SCI. These surfactants (Figure 4) are polysorbate 20, polysorbate 60, polysorbate 80, alkyl glucosides, PEG-n (n = 20–80) glyceryl stearates, PEG-n (n = 20–80) glyceryl isostearates, PEG-20–PPG-10 glyceryl stearates, PEG-n (n = 20–80) glyceryl oleates, PEG-n (n = 20–80) glyceryl cocoates, and PEG-n (n = 20–80) glyceryl laurates. Other non-ionic surfactants are less effective in this application. It should be emphasized that micelle stability is an essential element in shifting the SCI solubilization equilibrium to the right, thus increasing solubility. When a surfactant system consists of head groups that are similar to or larger and more complicated than those of SCI, micelle stability will increase and keep SCI dissolved.



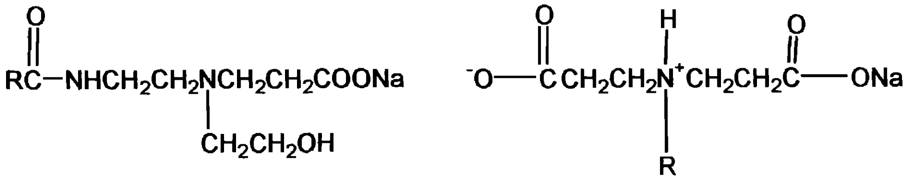
alkyl amidopropyl hydroxysulatine

sodium alkylamphoacetate



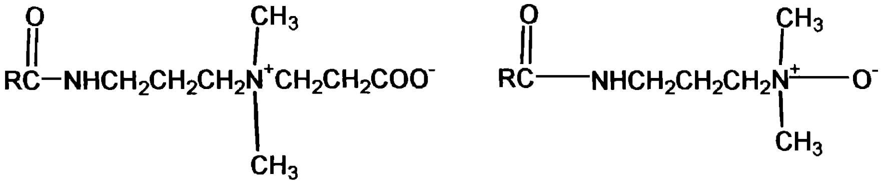
sodium alkylamphohydroxypropylsulfonate

disodium alkylamphodiacetate



sodium alkylamphopropionate

sodium alkyl iminodipropionate

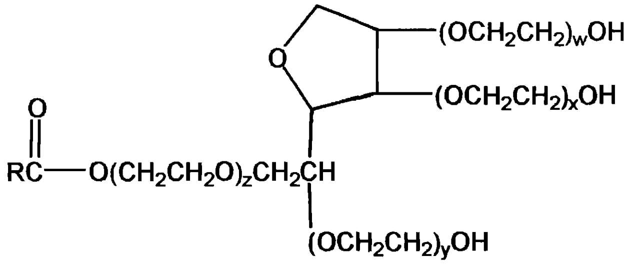


alkylamidopropyl betaine

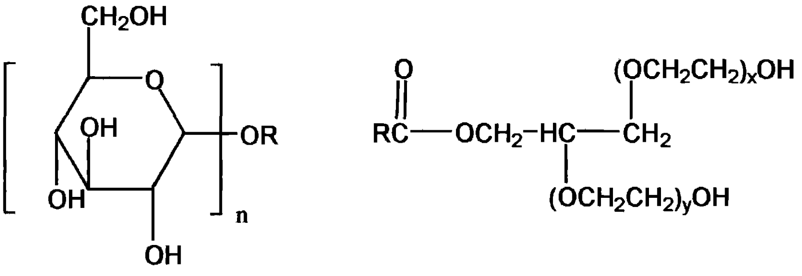
alkylamidopropylamine oxide

Figure 3. Structures of selected amphoteric surfactants.

Additionally, the concentration of CI^- within the average micelle decreases as secondary surfactant is added. When micelles in the stated equilibrium consist entirely of CI^-, an increase in the concentration of pure CI^- micelles will shift the equilibrium to the left, favoring the formation of solid SCI. However, if one disturbs the system such that the concentration of CI^- within micelles decreases, i.e., the micelles are no longer pure, then



polysorbate20, R=$C_{11}H_{23}$; polysorbate 60, R=$C_{17}H_{35}$; polycorbate 80, R=$C_{17}H_{33}$



alkyl polyglucoside **fatty acid monoglyceride ethoxylate**

Figure 4. Structures of selected non-ionic surfactants.

more aqueous CI^- will incorporate within these micelles, leading to greater SCI solubility. Thus the addition of secondary surfactants not only increases the strength of CI^- association with micelles, but also the number of aqueous CI^- molecules per micelle increases.

By introducing these selected surfactants, one can solubilize over 5–10% SCI in a clear detersive system. The following two examples illustrate some surfactants in such compositions. Based on the condition of mildness, the first example (Table I) can be used in a gentle facial cleanser and the second (Table II) is suitable for baby cleansing products.

Table I
Clear Detersive Formula of Selected Anionic Surfactants With 8% SCI

INCI name	Trade name	Percentage (%)
Sodium dioctyl sulfosuccinate	Mackanate EL® (30% active)	45.00
Sodium cocoyl isethionate	Hostapon SCI 85G® or Jordapon CI Prill®	8.0
Sodium cocoamphoacetate	Miranol Ultra C 37® (37% active)	4.0
Cocamide MEA	Amidex CME®	1.5
Thickener		q.s.
Preservatives		q.s.
Fragrance		q.s.
D.I. water		To 100%

Table II

Mild Baby Care Detersive Formula of Selected Non-Ionic Surfactants With 7% SCI

INCI name	Trade name	Percentage (%)
Polysorbate 20	Tween-20®	10.00
Polysorbate 80	Tween-80®	15.00
Sodium cocoyl isethionate	Hostapon SCI 85G® or Jordapon CI Prill®	7
Thickener		q.s.
Preservatives		q.s.
Fragrance		q.s.
D.I. water		To 100

It should be noted that as the formulation of cosmetics becomes more sophisticated, chemists will determine the geometric packing of micelles as standard practice, e.g., for spherical micelles, rods, and lamellar structures. It is known that as micelles proceed from spherical to lamellar formations, the density of micelles increases. As the density of micelles increases, the number of free CI^- ions decreases. This would push the solubility equilibrium to the right. Thus it is very likely that control of micelle formation also affects SCI solubility.

METHOD II: ION EXCHANGE

Even though some specialty surfactants efficiently solubilize SCI in aqueous solution (method I), they are often more expensive than common surfactants such as sodium lauryl sulfate (SLS) and sodium laureth sulfate (SLES), which do not efficiently solubilize SCI. For example, an aqueous solution of 10% SLS or SLES can only solubilize less than 1% of SCI and remain clear. Making more expensive formulas with specialty surfactants defeats the advantage of using a relatively inexpensive material like SCI. In order to incorporate SCI in affordable detersive systems for the mass market, the ion exchange method was developed through detailed examination of equilibrium (12).

The ion exchange method can prevent recrystallization of SCI by changing the total enthalpy of solvation from a positive to a negative value. Ion exchange is accomplished by adding ammonium ions from ALS and ALES, or triethanolamonium from TEALS and TEALES, all of which are significantly cheaper than the aforementioned specialty surfactants. The presence of free ammonium ions (or triethanolamonium) disrupts the ability of Na^+ to associate with CI^- ions and reform SCI. As was already stated, ACI and/or TEACI compounds have lower lattice energies and are more soluble. It thus becomes possible to keep more CI^- ions available to form micelles, which clean surfaces. Having more CI^- ions also favors interaction and substantivity to skin and keratin surfaces, allowing the user to experience the emolliency and moisturizing properties associated with this molecule.

It should be noted the formulator may choose ACI as a secondary surfactant despite the generation of free CI^- ions, which would normally shift equilibrium to the left. This is because the solubility contribution by the ammonium ion dominates the equilibrium; the reduction in lattice energy by ammonium outweighs any increase in aqueous CI^-.

Monoalkyl phosphate (MAP) surfactants will serve the same purpose. MAP surfactants have been studied extensively for their excellent foaming properties, exceptional mildness, and silky, talc-like afterfeel on skin or hair (6). Ammonium and triethanolamonium monoalkyl phosphate (AMAP and TEAMAP) are very soluble and able to increase the solubility of SCI. They are milder than ALS and ALES, but cost slightly more. In the same way, the ammonium salts of all the selected anionic surfactants in method I work much more efficiently than their corresponding sodium salts.

The ion exchange method makes it possible to include SCI as a primary surfactant in many liquid detersive compositions. This greatly decreases irritation normally associated with ALS and/or ALES. It is anticipated that chemists can thus make use of the excellent properties of SCI to the consumer's benefit. Table III illustrates this method.

METHOD III: EMULSIFICATION

Introduction of a small quantity of an emollient compound increases the solubility of SCI in water. This is mainly due to the previously mentioned attractive interaction between hydrocarbon tails and other molecules and to geometric packing constraints. As the quantity of oil increases in an SCI/water solution, CI^- will surround these droplets in the process of emulsification. As a result, the oil droplet becomes more stable as the emollient anchors the CI^- ions like liquid cement. As the droplet becomes larger, the number of aqueous CI^- ions that can associate with this body increases. Thus, stabilization via emulsified oil droplets and the uptake of CI^- work to shift equilibrium to the right, once again favoring the solubilization of SCI.

The most convenient way of employing this method is by using blends of emulsifying wax. These have non-ionic emulsifiers mixed with fatty esters or fatty alcohols. Those suitable for this application are: Polawax (emulsifying wax NF) from Croda; self-emulsifying Kester Wax K-82 H (INCI: C-20–40 alkyl stearates, ceteareth 20, and PEG-14 stearate) from Koster Keunen, Inc.; and Emulium Delta (INCI: cetyl alcohol, glyceryl stearates, PEG-75 stearate, ceteth-20, and steareth-20) from Gattefosse. One part of emulsifying wax NF will make three parts of SCI soluble in an emulsion. It is possible to have 30% SCI emulsified by 10% emulsifying wax NF to form an elegant facial cleanser. Since emollients are involved in this composition, only opaque liquid detersive systems can be formulated using method III. Table IV illustrates this application.

CONCLUSION

Three methods have been developed for solubilizing sodium cocoyl isethionate in aqueous detersive systems based on the understanding of enthalpy of solubilization, equi-

Table III
Clear Economic Detersive Formula of ALS and/or ALES Surfactants With 10% SCI

INCI name	Percentage (%)
Ammonium lauryl sulfate	7.00
Ammonium laureth sulfate	5.25
Cocamide MEA	1.75
Sodium cocoyl isethionate	10.0
Preservatives	q.s.
Fragrance	q.s.
D.I. water	To 100%

Table IV

Mild Detersive Formula of Emulsifying Wax With 30% SCI

INCI name	Trade name	Percentage (%)
Emulsifying wax NF	Polawax®	10.00
Sodium cocoyl isethionate	Hostapon SCI 85G® or Jordapon CI Prill®	30.00
Reology modifier		q.s.
Preservative		q.s.
Fragrance		q.s.
Water		To 100%

librium of solubilization, and the structures of SCI and other surfactants. These methods can be used individually or in combination. Chemists can use method I and III to make sulfate-free shampoos, body washes, and facial cleansers that are mild and have excellent afterfeel characteristics. Method II can be used to make inexpensive shampoos, body washes, and facial cleansers. These methods enable chemists to take advantage of the excellent properties associated with SCI in a variety of personal care applications at a reasonable price.

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