Making Homogeneous and Fine Droplet O/W Emulsions Using Nonionic Surfactants

HIROMICHI SAGITANI, Pola R&D Laboratories, Kanagawa-ku,
Takashimadai 27-1, Yokohama, Zip, 221, Japan

ABSTRACT

In many emulsion systems, creaming occurs during the first stage of emulsion breakdown. To reduce the rate of creaming, emulsions having small and uniform droplets are desirable. In this work, types and HLB of nonionic surfactants, emulsification methods, and combinations of oils and nonionic surfactants were investigated in order to make stable and homogeneous emulsions. Emulsification was attained by dissolving the surfactants in the oil phases. The addition speed and volume of water to the oil phases were important factors affecting the emulsion droplet size. The change of the solute state in the process of emulsification was observed stage by stage, and the mechanism of emulsification was elucidated. Homogeneous emulsions were formed in the HLB region, showing liquid crystalline and gel phases in the emulsifying process. The addition speed of water to the oil phase was very important in forming the liquid crystalline and gel phases. Polyoxyethylene(n)sorbitan monostearate could emulsify three kinds of oils (hydrocarbon, fatty acid ester and triglyceride). Polyoxyethylene(n)alkyl ether could emulsify hydrocarbon and fatty acid ester. Polyoxyethylene(n)-monostearate could emulsify only hydrocarbon. Surfactants with proper HLB which were soluble in the oil phase and in the presence of a very small amount of water formed a stable emulsion. The solubility state of oil and surfactant was the key to making a fine emulsion.

INTRODUCTION

Emulsions are widely used in creams, lotions and foundations in the cosmetic industry. The stability of emulsions has been studied by many investigators. Nevertheless, there are still many unsolved problems related to the manufacturing of emulsions and their stability during shelf life. For example, the physical characteristics of emulsions are not only dependent on their compositions, but also are strongly dependent on the technique of emulsification. Therefore, it is important to resolve these problems and elucidate the process of emulsification.

The purpose of this paper is to determine the mechanism of forming homogeneous and stable emulsions. For this purpose, the formation process of O/W emulsions was closely observed by using a simple model rather than a complex commercial cosmetic emulsion. The following items were considered as influencing factors for making fine emulsions: (a) nonionic surfactants, HLB of surfactants; (b) type of oils, hydrocarbon, ester and triglyceride; (c) method of emulsification, addition speed and volume of water to oil phase.

In cosmetics, a breakdown of emulsion is mainly caused by creaming. The velocity of creaming is defined by the Stokes' equation:

$$v=2gr^2(\rho_c-\rho_d)/9\eta,$$

where r = radius of droplet, ρ_d = density of droplet, ρ_c = density of bulk, η = viscosity of bulk. Therefore, a small droplet size is needed to prevent creaming. Correct adjustment of the HLB is important in order to have a small droplet emulsion (1). In nonionic surfactant emulsion systems, the stability of the emulsion is also related to the Phase Inversion Temperature (PIT). The smallest droplet size is obtained in the PIT region (2).

The type of oil influences emulsion conditions. Friberg showed the difference in stability between emulsions with aromatic and aliphatic hydrocarbons constituting the oil phase (3).

The technique of emulsification also affects emulsion stability. One of the factors in forming small and uniform emulsions is emulsification equipment. Another factor is physicochemical in nature. The physicochemical factor has to be considered in order to have a fine emulsion, no matter what kind of emulsification equipment is used.

The droplet size of O/W emulsions is strongly influenced by the method of incorporating the surfactant in the oil and aqueous phases. The agent-in-oil method usually results in more uniform emulsions than the agent-in-water method (4). Lin reported that emulsions prepared by initially placing the surfactant in the oil phase resulted in a more stable emulsion than a corresponding emulsion prepared by placing the surfactant in the aqueous phase (5,6).

In this paper, we investigated the emulsification mechanism by using the agent-in-oil method, and have elucidated the solubility state of the surfactants, oils and water systems on the emulsification process from phase diagrams.

EXPERIMENTAL

Materials

The oils and surfactants were cosmetic grade and used without further purification (Table I).

The surfactants used to determine the phase diagram were dehydrated in vacuo. It was confirmed that water content of the surfactant was less than 0.5% by Karl Fischer titration. Deionized and distilled water was used.

Procedure

Preparation of O/W emulsion. An oil solution (25 g) containing 20 wt % nonionic surfactants was placed in a 200-ml beaker and heated to 60 C to melt. Water (75 g), heated to the same temperature, was added to the oil phase with stirring. Initially, the water was added very slowly until a liquid crystalline phase was formed. The second portion of water was added rapidly until a white gel phase was formed. Finally, the last portion was added slowly. After addition was completed, the emulsion was further stirred for 10 min at 1,000 rpm and cooled from 60 to 20 C in a water bath of 0 C. This emulsification procedure is called the inversion emulsification method.

The emulsion droplet size was observed under a microscope (olympas optical). The stability of the emulsion formed was determined from the degree of creaming after 1 week in a thermostated room at 25 ± 3 C.

The operation of emulsification was done in an enclosed system to prevent evaporation. Nevertheless, the water content decreased 2-3 wt % by evaporation in the process of emulsification. It was confirmed that emulsion stability and mean droplet size were not affected by the reduction of 5 wt % water.

Phase diagram of nonionic surfactants/liquid paraffin/water system. The liquid paraffin solution containing 20 wt % nonionic surfactants was first placed in a 13-mm pyrex

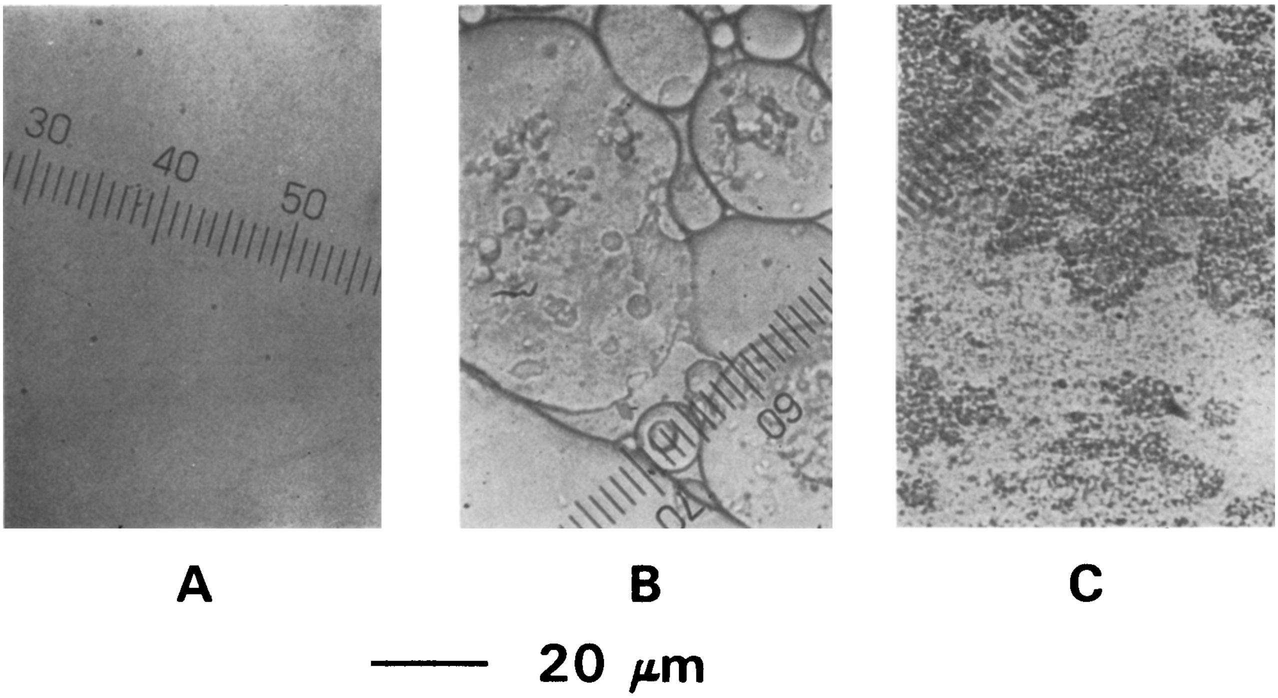

FIG. 2. Effect on droplet size by three emulsifying methods: sorbitan monostearate, 1.6 (wt %); POE (20 sorbitan monostearate, 3.4; liquid paraffin, 20; water, 75. A had water added gradually, and emulsified by the inversion emulsification method. B had water added quickly. C had water added quickly, and emulsified by homomixer with 10,000 rpm for 10 min.

is found in the region of HLB number 11.2-12.4. This HLB region also gives liquid crystalline and gel emulsion phases. To make a fine and homogeneous emulsion, it is necessary to pass through liquid crystalline and gel emulsion phases in the process of emulsification.

Alkyl-ether-type nonionic surfactant. The solubility of 20 wt % POE cetostearyl ether liquid paraffin solution and water is shown in Figure 5. The HLB was adjusted by mixing POE (5.5, 7 and 10) cetostearyl ether. O, L.C. and gel emulsion regions were also observed in the ether-type nonionic surfactant system. In this system, the peak of the O and L.C. regions were closer than in the sorbitan-type surfactant system. POE cetostearyl ether has a stronger affinity for liquid paraffin, and therefore, it could dissolve in liquid paraffin without water.

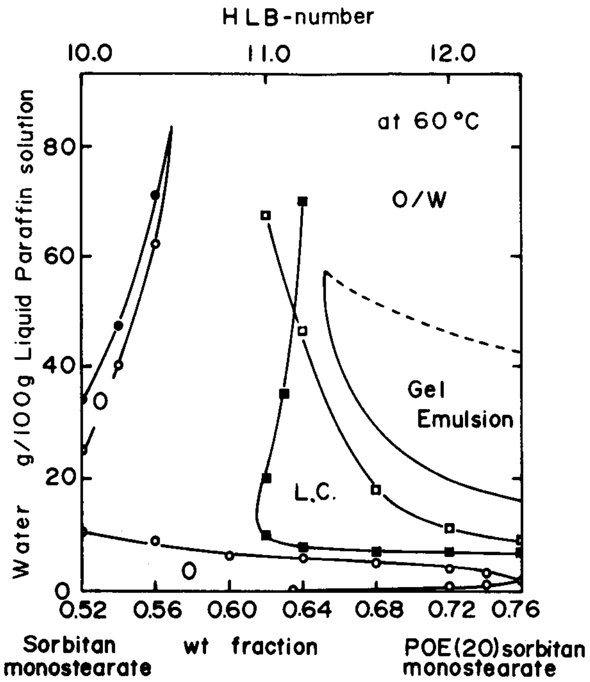

FIG. 3. Effect of added water on the solubility state of liquid paraffin solution containing 20 wt % sorbitan monostearate and POE (20) sorbitan monostearate. O:oil continuous phase; L.C.: liquid crystalline phase.

Ester-type nonionic surfactant. The solubility of 20 wt % POE stearate liquid paraffin solution and water system is shown in Figure 6. POE stearate has a weaker affinity for liquid paraffin than POE cetostearyl ether. It cannot dissolve in liquid paraffin in the HLB region for an O/W emulsion. However, hydrated POE stearate can dissolve. The gel structure is weaker than for the POE sorbitan monostearate or POE cetostearyl ether systems. A liquid paraffin phase separated from the gel phase upon standing for a week.

Preparation of O/W Emulsions with Higher Molecular Nonionic Surfactants

The emulsifying ability of high molecular nonionic surfactants is weaker than that of normal surfactants, but they have a high stabilizing power against coalescence (9) and a low skin stimulus (10). Recently, high molecular surfactants have been used as emulsifiers. In this paper, the emulsification characteristics of hydrogenated castor oil POE adducts and POE-POP stearyl ether were investigated.

Hydrogenated Castor Oil POE Adducts

Emulsification of the liquid paraffin/water sytem was tried using hydrogenated castor oil POE (5, 10, 20, 30, 40, 50, 60 and 80) adducts. These surfactants did not dissolve in liquid paraffin in either the dried or hydrated state. A liquid crystalline and gel phase did not exist in any HLB region. Consequently, hydrogenated castor oil POE adducts could not emulsify the liquid paraffin/water system.

TABLE I

Materials

Type	Nonionic surfactants compound	Abbreviation	Manufacturer
Sorbitan monostearate	Sorbitan monostearate	Sorbitan monostearate	Toho Chemical
	Polyoxyethylene (20) sorbitan monostearate	POE (20) sorbitan monostearate	Toho Chemical
Alkyl ether	Polyoxyethylene(n)cetyl ether/ polyoxyethylene(n)stearyl ether (6:4 mixture)	POE (n) cetostearyl ether	Nikko Chemical
	Polyoxyethylene (n)/ polyoxypropylene (18) stearyl ether	POE (n)-POP (18) stearyl ether	Nissan Chemical
Ester	Polyoxyethylene-(n)-stearate	POE (n) stearate	Nikko Chemical
	Hydrogenated castor oil ethylene ethylene oxide adduct		Nikko Chemical
	Oils		
Hydrocarbon	Liquid paraffin (vis. 13.65 cST, at 37.8 C)		Esso Standard
Ester	Isopropyl myristate		Nikko Chemical
Triglyceride	Glycerol tris,(2-ethyl)hexanoate		Nisshin Seiyu

test tube with teflon sealed screw cap, and water was added at increments, equivalent to 1 wt % of the oil phase. These test tubes were kept at 60 ± 0.5 C for 1 week with occasional shaking. The solubility state was then observed. The solutions with a high viscosity were put into a high temperature water bath to reduce viscosity, then cooled to 60 C with shaking. Liquid crystals were observed using a polarized prism.

Measurement of apparent viscosity and emulsion particle size. The apparent viscosity of the liquid crystal, gel and emulsion was measured at 60 C at a maximal shear rate of 268 sec^{-1} with a cone-plate-type viscometer (Meisei Electric Co.). The particle size of the emulsion was measured immediately after emulsification under a microscope at 600 X magnification. The emulsions having small particles were diluted ca. 10-20 times with water. The mean value of the particle diameter was calculated by counting 100 emulsion droplets.

RESULTS

Preparation of Homogeneous O/W Emulsion

A general emulsification method for making cosmetic emulsion is as follows. The oil phase containing oil, wax and emulsifier is melted in a heating bath. Then the water phase at the same temperature is added to this oil phase with stirring. The emulsion is cooled to room temperature. This method of emulsification was adopted in this study. The flow diagram for emulsification is shown in Figure 1.

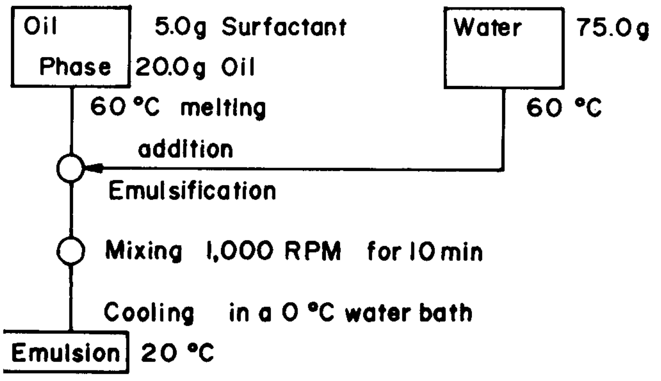

FIG. 1. Flow chart of emulsification.

Even though all O/W emulsions were made under the same conditions, some emulsions had different droplet sizes and stability due to the difference in the rate of water addition. The photomicrographs of emulsions made by three different emulsifying methods are shown in Figure 2. These three emulsions have identical compositions, but the mean droplet size of emulsion A is very small, that of emulsion B is large, and that of emulsion C is intermediate. Emulsion A was emulsified by the method described in Experimental. In emulsion B, water was added quickly. Emulsion C was formed by adding water quickly, then was emulsified by a homogenizer at 10,000 rpm for 10 min. The first emulsification method was more effective in obtaining a homogeneous emulsion than the others. To show this difference, the change of the solubility state of the surfactant-oil-water system during the process of emulsification was investigated.

Solubility State of Three Types of Nonionic Surfactants/Liquid Paraffin/Water System and the Procedure of Emulsification

Sorbitan-monostearate-type nonionic surfactant. The change of the solubility state of the liquid paraffin solution containing 20 wt % sorbitan monostearate and POE(20) sorbitan monostearate vs water volume is shown in Figure 3. The numbers on the abscissa indicate the weight fraction of sorbitan monostearate and POE(20) sorbitan monostearate and HLB number as given by the method of Griffin (7). The surfactants that were rich in sorbitan monostearate dissolved in liquid paraffin, but the surfactants rich in POE(20) sorbitan monostearate did not dissolve. If a small amount of water is added to this solution in the range of HLB number 11.1-12.3, the surfactant dissolved in liquid paraffin with no detectable association (8). The volume of water solubilized in liquid paraffin increased greatly in a very narrow HLB region. This HLB number is ca. 10.5. The HLB of this system is nearly balanced at this point. An O/W emulsion was obtained in the more hydrophilic region rather than at the HLB, which gave the maximal solubilization of water. In the hydrophilic region, a liquid crystalline phase (L.C.) separated from the oil phase when water was added beyond the solubilization region.

The relationship between droplet size of the O/W emulsion and the ratio of sorbitan monostearate and POE(20) sorbitan monostearate is shown in Figure 4. The O/W emulsion having small and homogeneous droplet size

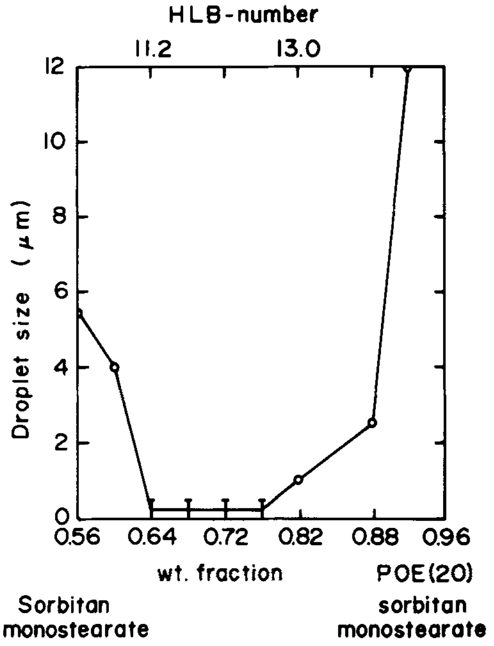

FIG. 4. The relationship between HLB number and droplet size emulsified by combination of sorbitan monostearate and POE (20) sorbitan monostearate. The emulsion system is surfactants/liquid paraffin/water (5:20:75 wt).

Because castor oil is difficult to dissolve in liquid paraffin, such a combination of the surfactant and oil is unsuitable for an emulsion system. When the liquid paraffin was replaced with isopropyl myristate, hydrogenated castor oil POE (40, 50 and 60) adducts could form homogeneous emulsions. There were liquid crystalline and gel phases also in this system. Figure 7 shows the solubility of hydrogenated castor oil POE adducts and isopropyl myristate in relation to temperature and number of ethylene oxide unit. Hydrogenated castor oil was used with 20, 30 and 40 mol of ethylene oxide dissolved in isopropyl myristate. As the length of the ethylene oxide chain increased, the solubility temperature increased and reached a maximum. It is believed that this effect results from hydrogen bonding and the dipole moment between the surfactant and oil. On the other hand, the melting point increased with the length of the ethylene oxide chain. Therefore, a transparent solution was obtained in the region between the solubility and melting curves. Hydrogenated castor oil POE adducts do not dissolve in nonpolar hydrocarbons in any HLB region, because nonpolar hydrocarbons do not have any dipole attraction to the surfactant. But, isopropyl myristate has a dipole moment and hydrogen bonds to the surfactant. Therefore, it is difficult to emulsify nonpolar oils by a surfactant in which the hydrophilic group is not located at the end of the molecule.

POE-POP Stearyl Ether

In POE-POP alkyl ether nonionic surfactants, the number of propylene oxide units does not have a great effect on cloud point or HLB (11,12). The emulsification of the systems was investigated using POE (7, 20, 30 and 35)-POP (18) stearyl ether. These surfactants have a terminal hydrophilic group, so they will be suitable for emulsifying nonpolar hydrocarbons. POE-POP stearyl ether was used with 30 mol of ethylene oxide unit dissolved in liquid paraffin in the hydrated state. A gel phase also existed in the emulsifying process. Stable emulsions were obtained with 30 and 35 mol ethylene oxide adducts. On the other hand, all the surfactants could not emulsify the isopropyl myristate/water system because they had a high affinity to polar oil and dissolved in oil at any HLB.

Effect of Combination of Oil and Surfactant on Emulsification

As already mentioned, the combination of oil and surfactant is important, and some combinations can not emulsify at any HLB. Liquid paraffin (nonpolar hydrocarbon), isopropyl myristate (ester), and glycerol tris, (2-ethyl) hexanoate (triglyceride) were selected as oils. POE sorbitan monostearate, sorbitan monostearate, POE cetostearyl ether, POE stearate, hydrogenated castor oil POE adducts and POE-POP stearyl ether were selected as surfactants.

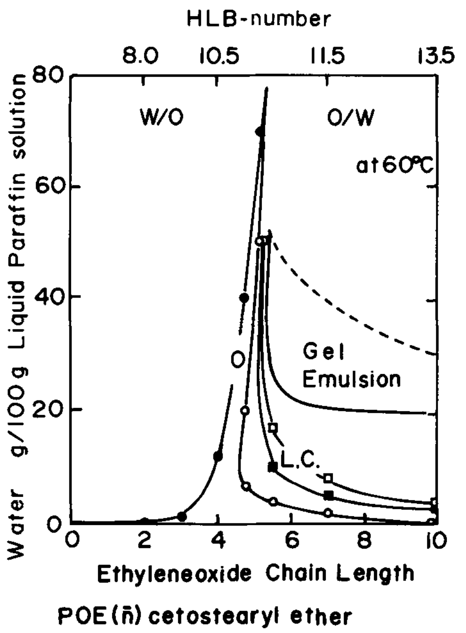

FIG. 5. Effect of added water on the solubility state of liquid paraffin solution containing 20 wt % POE (n) cetostearyl ether.

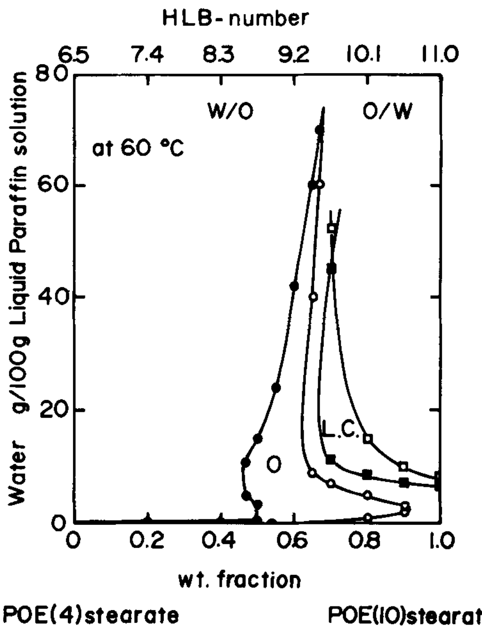

FIG. 6. Effect of added water on the solubility state of liquid paraffin solution containing 20 wt % POE (4) stearate and POE (10) stearate.

These oils and surfactants were combined and emulsified. The number of ethylene oxide units and HLB number giving the most stable emulsions are shown in Table II.

Sorbitan monostearate could emulsify the three types of oils. Ether surfactants could emulsify hydrocarbons and esters. Ester surfactants could emulsify only hydrocarbons. The HLB giving a stable emulsion was lower in hydrocarbon than in polar oil. This result agrees with the change of PIT (4). POE-POP stearyl ether dissolved in isopropyl myristate and glycerol tris, (2-ethyl)hexanoate, but did not make a gel in the process of emulsification or a stable emulsion.

DISCUSSION

To obtain a stable emulsion, the surfactants must dissolve in the oil phase in a dried or hydrated state. Even if the surfactants dissolve in the oil phase, they cannot give stable and homogeneous emulsions if they do not form liquid crystalline and gel phases in the process of emulsification. The liquid crystal can involve much oil and water. There is no oil phase in this liquid crystalline region. It was observed by a cone-plate viscometer that this liquid crystal had a dilatant hysteresis loop. When water was added beyond the liquid crystalline phase, a white gel phase which had a thixotropic hysteresis loops, respectively (13). It was reported that a lamellar phase appeared when water was added beyond the oil continuous region (3,14,15). The gel is a dispersion system of oil in an isotropic gel phase. Lachampt and Vila presented the phase diagrams of POE oleyl ether/water/liquid paraffin systems. They showed that the isotropic gel phase appeared when liquid paraffin was added to the hexagonal liquid crystalline phase, and considered the isotropic gel in which the oil entered between the lipid chains of the hexagonal phase (14,15). The structure of the isotropic gel phase is not clear, but it seems to be akin to hexagonal. Tsugita et al. also showed the existence of the white gel in the isotropic gel and oil two-phase region (16).

The lamellar phase is a region where the HLB of a component system is optimal (17). This liquid crystalline phase approaches the oil phase at the maximal solubilization point. The HLB is also optimized at this point. This region forms a minimal curve against HLB number. This result is similar to an Emulsion Inversion Point (18). Shinoda reported that the droplet size of O/W emulsion and the interfacial tension had a minimum at the PIT range (2,11). A stable O/W emulsion was obtained at 20-65 C lower temperatures than the PIT. Solubilization has a maximum in the PIT range, and therefore, the HLB is optimal in this range. This result shows that a fine and stable O/W emulsion is formed at a slightly hydrophilic range of optimal HLB. Bourrel et al. showed the relationship of microemulsion (optimal HLB) and interfacial tension (19). Microemulsion is formed in the maximal range of solubilization (20). Interfacial tension will have a minimum at the lamellar liquid crystalline region from Winsor's theory (17). In our emulsification process, the liquid crystal gives one phase, and there is no oil droplet in this region. When the lamellar phase changes to the gel phase, the oil phase separates from the surfactant phase, but the water remains in the phase. The required HLB shifts to a more hydrophilic value as water is added. The interfacial tension between the oil and surfactant phases will still be very low, so very small oil droplets are formed as O/D (oil-in-surfactant) emulsion. This agrees with the results reported by Shinoda. The highly viscous gel prevents coalescence and helps the droplets disperse uniformly. The

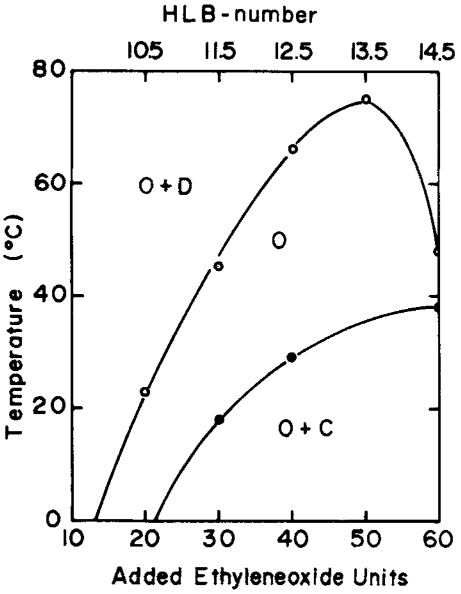

FIG. 7. Solubility state of isopropyl myristate solution containing 20 wt % hydrogenated castor oil ethylene oxide adducts. : melting point; ○: solubility point.

TABLE II

Effect of Combination of Surfactants and Oils for Forming Stable O/W Emulsions

Oil	Surfactant	n	HLB number	Emulsion
Liquid paraffin	POE sorbitan monostearate	12.8	11.2	stable
	POE cetostearyl ether	5.5	10.5	stable
	POE stearate	8.8	10.1	stable
	Hydrogenated castor oil POE adduct			no emulsification
	POE-POP stearyl ether	30		stable
Isopropyl myristate	POE sorbitan monostearate	14	11.8	stable
	POE cetostearyl ether	7	11.5	stable
	POE stearate	13	11.8	unstable
	Hydrogenated castor oil POE adduct	60	14.0	stable
	POE-POP stearyl ether			no emulsification
Glycerol tris, (2-ethyl)hexanoate	POE sorbitan monostearate	14	11.8	stable
	POE cetostearyl ether	8.2	12.3	unstable
	POE stearate			no emulsification
	Hydrogenated castor oil POE adduct	50	13.5	stable
	POE-POP stearyl ether			no emulsification

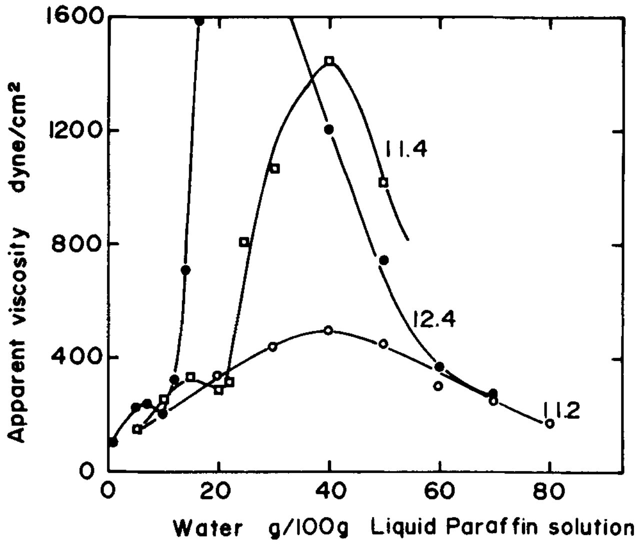

FIG. 8. Effect of added water and HLB number on apparent viscosity of liquid paraffin (80 wt %)/sorbitan monostearate+POE (20) sorbitan monostearate (20 wt %) system. The numbers in the figure represent HLB number; at 60 C, the shear rate was 268 sec^{-1}.

gel phase changes continuously to an aqueous phase by further addition of water. Homogeneous O/W emulsions can be formed by this process, i.e., oil continuous phase → liquid crystalline phase → white gel phase → O/W emulsion (Fig. 8).

A simple method for learning whether surfactants are suitable as emulsifiers for a given oil phase follows. First, examine the solubility of surfactants in the oil phase. The surfactant must dissolve in the oil phase at a suitable HLB region in the hydrated state. If a liquid crystalline or gel phase appears in the process of adding water, a homogeneous emulsion will be obtained.

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Hydrotropic Action of a Diacid

J.M. COX and **S.E. FRIBERG**[1], Department of Chemistry,
University of Missouri-Rolla, Rolla, MO 65401

ABSTRACT

An investigation to evaluate the mechanism of the hydrotropic action of a long chain diacid was made by determining the coassociation structures with a straight chain amphiphilic molecule of sufficient size to form long range order structures. The hydrotropic mechanism was found in the transition of a liquid crystalline structure to an isotropic solution. The mechanism was identical for aqueous solutions and water-poor inverse micellar solutions.

INTRODUCTION

A class of substances named hydrotropes (1) possesses the property of increasing the solubility of poorly water soluble substances to an extreme degree when added to water in high concentrations. The typical solubility increase is from a fraction of a percent to the magnitude of 50% by weight when the level of hydrotrope reaches 25-30% by weight. A great number of researchers (2-6) have studied the shape of these solubility curves relating them to the structure of the hydrophobic part of the hydrotrope.

Friberg and Rydhag (7) showed the hydrotropic action to be coupled with long range order amphiphilic association structures. The higher solubilization capacity by a hydrotrope (≅60%) compared to that by a common surfactant (≅10%) was shown to depend on one fact: the isotropic solution of the hydrotrope was not changed to a liquid crystalline phase when a long chain hydrophobic amphiphile was added. This meant that the "cut-off" of the aqueous micellar solubilization that occurs with amphiphiles by normal surfactants (8) did not take place; the isotropic solution continued toward high concentrations of the amphiphilic substance. This mechanism was useful to explain the hydrotropic action of the low molecular weight hydrotropes such as the common sodium xylene sulfonate (7).

Recently, a new class of hydrotropes has been introduced (9-11) with Westvaco DIACID®, 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid. This compound consists of a long hydrocarbon chain with a total of 21 carbon atoms and the difference in structure is pronounced from the conventional hydrotropes such as the xylene sulfonates. Since the diacid has proven to be an efficient hydrotrope, we found basic investigation on the mechanism for its

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[1] To whom correspondence should be addressed.