CHAPTER II

MICROEMULSION FORMATION AND DETERGENCY WITH
OILY SOILS: I. PHASE BEHAVIOR AND INTERFACIAL TENSION

ABSTRACT: The ultimate objective of the project is to investigate the relationship between microemulsion phase behavior and detergency for oily soils. In this part of the study, surfactant phase behavior was evaluated for hexadecane and motor oil as model oily soils. Producing microemulsions with these oils is particularly challenging because of their large hydrophobic character. To produce the desired phase behavior we included three surfactants with a wide range of hydrophilic/lipophilic character: alkyl diphenyl oxide disulfonate (highly hydrophilic), dioctyl sodium sulfosuccinate (intermediate character), and sorbitan monooleate (highly hydrophobic). This mixed surfactant was able to bridge the hydrophilic/lipophilic gap between the water and the oil phases, producing microemulsions with substantial solubilization and ultralow interfacial tension. The effect of surfactant composition, temperature, and salinity on system performance was investigated. The transition of microemulsion phases could be observed for both systems with hexadecane and motor oil. In addition, the use of surfactant mixtures containing both anionic and nonionic surfactants leads to systems which are robust with respect to temperature compared to single surfactant systems. Under conditions corresponding to "supersolubilization", the solubilization parameters and oil/microemulsion interfacial tensions are not substantially worse than at optimum condition for a middle phase system, so a middle phase microemulsion is not necessary to attain quite low interfacial tensions. A potential drawback of the formulations developed here is that a fairly high salinity (e.g., 5 wt% NaCl) is needed to attain optimum middle phase systems. The correlation between interfacial tension and solubilization follows the trend predicted by the Chun Huh equation.

KEY WORDS: surfactant mixture, microemulsion, motor oil, alkyl diphenyl oxide disulfonate, dioctyl sodium sulfosuccinate, sodium monooleate, phase behavior

INTRODUCTION

Microemulsions are thermodynamically stable systems consisting of water, oil and surfactant. Microemulsions can have remarkable properties. Low surfactant concentrations (a few wt%) can produce a phase containing equal volumes of oil and of water. Extremely low interfacial tensions between water and oil phases can be associated with microemulsions (e.g., a factor of 10^4 lower than ordinary phase oil-water interfacial tensions). Schulman and Cockbain first reported the characteristics of microemulsions in the 1940s (1). While in application microemulsions are often formed using multiple component systems, single surfactant systems are widely evaluated in phase behavior studies since they are simple to conduct and make it possible to examine a wide range of variables. While microemulsion formation often requires additives beyond the surfactant alone, under select conditions single surfactant systems have been reported to form microemulsions without any cosurfactants or additives; e.g., Aerosol OT with twin tails (2). Additives for enhancing microemulsion formation include cosurfactants, cosolvents, electrolytes, hydrotropes, and linkers. Important properties of microemulsion are high solubilization capacity for oil and ultralow interfacial tension (IFT) between oil and water.

Of particular interest to this project is the role of linker molecules in formulating microemulsion systems (3,4,5,6,7,8,9). A linker molecule is an amphiphilic molecule that enhances the interaction between the surfactant and oil (A_{CO} interaction, e.g. a lipophilic linker), or the interaction between the surfactant and water (A_{CW} interaction, e.g. a hydrophilic linker). Most lipophilic linkers are long chain fatty alcohols or ethoxylated secondary alcohols with one or two ethoxy groups (4). For the case of hydrophilic linkers, they are surfactant like molecules with 6-9 carbons in the hydrophobic tail per hydrophilic headgroup (7). By combining linker molecules we can extend the interaction of the surfactant with water (A_{CW}) and oil (A_{CO}), thus providing a more efficient way to bridge the hydrophilic-lipophilic gap between the surfactant and oil than using a single surfactant molecule.

Typical phase diagrams of a surfactant / water / oil system are illustrated in Figure 1 and Figure 2 in terms of microstructure and IFT of the system. When the microemulsion properties are changed by varying a single parameter, the resulting

graph is known as a "scan". Electrolyte concentration is commonly used as the scan variable for microemulsion system when ionic surfactants are present, while temperature is often used for nonionic surfactant systems. In either case, as the scan variable increases (salinity or temperature), the water solubility of the surfactant decreases and oil solubility increases. One way to characterize this water solubility is through the hydrophile-lipophile balance or HLB number; a higher HLB indicates higher water solubility (10).

The microemulsion "phase" is that which contains most of the surfactant. At high HLB values, on the left-hand side of Figure 1, the surfactant is predominantly in the water phase, which is in equilibrium with an "excess" oil phase having a very low surfactant concentration. This is known as a Winsor type I microemulsion or sometimes W_m or an O/W microemulsion since the water is the continuous phase. In this region, the IFT between excess oil and O/W microemulsion decreases as the HLB at the interface of the system decreases. At an appropriate HLB, the system splits into three phases: an excess water phase with low surfactant concentration, a middle phase or microemulsion phase, and an excess oil phase with low surfactant concentration. This new third phase is called a Winsor type III microemulsion system. The interfacial tension in the region of middle phase or Winsor type III is often as low as 10^{-3} mN/m or so-called ultralow interfacial tension. The lowest value of interfacial tension, which is called the optimum interfacial tension (IFT*), is at the point where the IFT between the excess oil and the middle phase ($IFT_{O/M}$) intersects with the IFT between the middle phase and the excess water ($IFT_{W/M}$).

The region of type I close to the transition region from type I to type III is known as supersolubilization region (see Figure 2) (11). In this region, micelles are swollen due to high solubilization of oil. For some systems, hazy or milky but translucent solution appears at the system close to this transition zone. Even though the IFT in the supersolubilization region is not as low as at the optimum conditions in a type III system, supersolubilization still provides considerably higher solubilization as well as low interfacial tensions without formation of a middle phase. Supersolubilization was first mentioned in the area of surfactant enhanced remediation because it is believed to be able to overcome the problem of downward migration of DNAPL (Dense Nonaqueous Phase Liquid) mobilized by ultralow

interfacial tension in the type III system (12). As we will discuss later, while low oil/water interfacial tensions and high aqueous phase solubilization of oily soils are desirable in detergency, the presence of a middle phase may also be undesirable in that application; hence the potential relevancy of the supersolubilization region becomes a candidate for these two applications. As the HLB is further decreased from a type III system (far right-hand side of Figures 1 and 2), the system again is composed of two phases; an oil phase microemulsion in equilibrium with an excess water phase. This is a Winsor type II microemulsion or sometimes O_m or a W/O microemulsion.

For whichever phase is the microemulsion (contains most of the surfactant) the solubilization parameter (SP) is the volume of oil or of water per weight of surfactant in the microemulsion phase. For the Winsor type III system, when the volume of oil and the volume of water solubilized in the middle phases are equal, this corresponds to the same composition at which the optimum interfacial tension is attained (IFT*). At this optimum composition, SP is referred as SP*. Later in this paper, we will describe a mathematical relationship between IFT and SP. Since essentially all of the surfactant is in the microemulsion phase (13) and a significant amount of oil is solubilized in the excess water phase or water in an excess oil phase (the excess phase containing very low surfactant concentration), the value of SP can be calculated by measurement of the relative phase volumes in the microemulsion phase at equilibrium. Since this is much easier to measure than interfacial tensions, optimum conditions and the region of supersolubilization are often characterized from SP values. If salinity (added NaCl concentration) is the scan variable being changed, the salinity corresponding to IFT* or SP* is optimum salinity or S*.

The relationship between microemulsion formation and detergency has been established for decades (14,15,16). Several studies have evaluated the role of interfacial tension reduction for soil removal on fabric by nonionic surfactants (17,18,19). Microemulsion formation is believed to enhance detergency due to emulsification and solubilization mechanisms. Tungsubutra and Miller (20) stated that, for synthetic fabrics, greater adhesion between fabric and soil makes the rollback mechanism ineffective, and oil removal occurs mainly by a solubilization-emulsification mechanism. Emulsification-solubilization and rollback are considered

to be the dominant mechanisms in oily soil detergency. The solubilization of oily soil depends on several factors, such as nature of oil and surfactant, surfactant concentration, electrolyte concentration, temperature, etc.

Motor oil is complex in composition, and is highly hydrophobic. It generally consists of at least five main components: (a) n-parrafins, (b) isoparaffins, (c) cycloparaffms, (d) aromatic hydrocarbons, and (e) mixed aliphatic and aromatic ring compounds. In addition to these five components, several additives are commonly added to the oil to act as a rust inhibitor, oxidation inhibitor, detergent-dispersant, viscosity-index improver, pour-point dispersant, and antifoam, (21). The EACN (equivalent alkane carbon number) is a parameter used to characterize the hydrophobicity of the oil. It is an equivalent number of carbons in a complex mixed oil as compared to a single component alkane oil. A high EACN signifies a high hydrophobicity of the mixed oil. Wu and Sabatini (22) used an alcohol partition method to determine EACN values of several oils including motor oil. Wu *et al.* (23) further studied and reported the EACN value of their motor oil to be 23.5. Hexadecane or cetane, whose ACN (Alkane Carbon Number) is 16, was studied in this research since it is a typical long chain alkane hydrocarbon and widely used as oily soil in detergency tests.

While traditionally the formulation of emulsions and microemulsions have been done in the framework of the HLB concept, this concept only indicates that the combined HLB of the surfactant system must match that of the oil. With the linker approach to microemulsions it has been proposed that the best method is to select a surfactant of intermediate HLB (not necessarily close to that of the oil) and adjust the concentration of hydrophilic and lipophilic linker that gives the best microemulsion performance. The hypothesis of this work is that by combining a very hydrophilic surfactant (ADPODS, similar to a hydrophilic linker), with a very hydrophobic surfactant (Span 80, similar to a lipophilic linker) and a surfactant of intermediate HLB, AOT (24) we can obtain middle phase microemulsion with substantial solubilization and ultralow interfacial tension. ADPODS used for this study is C_{16} diphenyl oxide disulfonate which is reported to has HLB number higher than 41 (25).

Alkyl diphenyl oxide disulfonate or ADPODS was selected in this study as the hydrophilic surfactant because of its high performance in particulate soil removal

and excellent hardness tolerance (17). ADPODS has been studied in enhanced oil recovery (EOR) due to its resistance to precipitation and adsorption (12). Basically, the highly hydrophilic nature of ADPODS, which results from its twin sulfonate head groups, makes it difficult to form microemulsions, especially for more hydrophobic (higher EACN) oils. Therefore, in this research, other surfactants were combined with ADPODS to promote microemulsion formation with hexadecane and motor oil. Sorbitan monooleate is a nonionic surfactant proposed for enhancing oil solubilization. Since ADPODS and sorbitan monooleate (Span 80) are very different in HLB, a third surfactant with an intermediate HLB, dioctyl sodium sulfosuccinate (AOT), was introduced into the system.

The advantages of using surfactant mixtures in industrial applications are widely known, as illustrated by the use of the mixtures containing nonionic surfactants having different chain lengths or different numbers of ethoxylated groups (26). Mixed surfactant systems generally have greater solubilization than single surfactant systems (27). Surfactant mixtures have been also employed for microemulsion formation and enhancing solubilization for several types of oils (27).

As temperature increases, the HLB of anionic nonethoxylated surfactants increases while the HLB of ethoxylated nonionic surfactant decreases (28) Due to this opposite impact of temperature, mixtures of anionic and nonionic surfactants are expected to be able to reduce temperature effects on microemulsion type transitions and produce more temperature-robust systems. Salager et al. (29) reported that a given optimum salinity of mixed surfactant systems corresponded to different ratios of mixed surfactants, depending on the system temperature. However, at a given ratio of mixed surfactants, the system was temperature insensitive over a wide range of temperatures (20-70°C). Anton et al. (30) further evaluated several surfactant mixtures to investigate the optimum formulation that most dramatically reduced temperature sensitivity. Binks et al. (31) also investigated temperature sensitivity of surfactant mixtures, and proposed a phenomenological model to relate the mole ratio of the mixture to molecular structure, solubilization, phase inversion temperature and interfacial tension. The model was formulated by using a mixing rule concept to define composition or weight fraction ratio of ionic surfactant system in the mixed nonionic and ionic surfactants to obtain temperature-insensitive microemulsions.

The model values agreed quite well with the experimental results, except at high interfacial tensions.

Besides the formation of microemulsions (Winsor type I, III and II) other phases e.g. lamellar liquid crystal (L_α) or sponge (D') can also occur, especially at high surfactant concentrations. Therefore, to obtain the desired type of microemulsion for any particular application, a systematic study has to be carried out for the surfactant formulation. The objectives in this first part of the study were to investigate the phase behavior of the mixed surfactants with hexadecane and motor oil. The effects of the electrolytes as well as the hydrophilicity and lipophilicity of each surfactant on phase behavior were investigated. In addition, solubilization and interfacial tension of the systems were examined. In Part II of this study, detergency results will be correlated to this phase behavior. In part III, more details concerning detergency mechanisms will be presented.

EXPERIMENTAL PROCEDURES

Materials. The alkyl diphenyl oxide disulfonate (ADPODS) used in this research was a commercial grade anionic surfactant supplied by Dow Chemical Co. known as Dowfax 8390 (Midland, MI, USA). Dowfax 8390 consists of C_{16} diphenyl oxide disulfonate as a major component. Dioctyl sodium sulfosuccinate was purchased from Fisher (Fair Lawn, NJ, USA) as AOT (100% solid). Sorbitan monooleate was obtained from ICI Uniquema Co. (Wilmington, DE, USA) as Span 80. Properties and selected characteristics of the surfactants are shown in Table 1. The oils used in the experiment were hexadecane and motor oil. Hexadecane was purchased from Aldrich (99% purity) (Milwaukee, WI, USA). The motor oil is commercially available for use in gasoline engines, type SAE 10W-30 (Castrol GTX). As the motor oil used in this study is a commercial product and may vary in composition, the same batch of oil was used throughout this research work. All chemicals were used as received without any further purification.

Phase studies were prepared by first adding an aqueous surfactant solution in flat bottom screw cap tubes. Then the oil was added at a water to oil volumetric ratio of unity. When surfactant concentrations are reported (e.g., 3 wt% AOT), these are based on the total mass in the system (water + oil + surfactants + electrolyte). The

of unity. When surfactant concentrations are reported (e.g., 3 wt% AOT), these are based on the total mass in the system (water + oil + surfactants + electrolyte). The solutions were well shaken and left in the water bath for equilibration at 25°C. Equilibrium took from 1 day to a few weeks depending upon the formulation composition. Phase volumes were measured to determine the solubilization parameter (S*). Interfacial tensions between equilibrated phases were measured by a University of Texas Spinning Drop Tensiometer, Model 500.

The value of S* was obtained after observing the phase behavior of the tubes set in an incubation bath at a given temperature from 20 to 60 °C. Phase volumes were measured upon equalization and S* values were determined at the point where the solubilization parameter of water equals the solubilization parameter of oil. *The surfactant weight fraction (X$_i$) refers to the weight of the variable surfactant (i) divided by the total weight of surfactants.*

RESULTS AND DISCUSSION

Phase behavior with salinity scan. Salinity scan results for the systems with hexadecane and motor oil are presented in Figure 3 for the surfactant mixtures 3 wt% AOT, 2 wt% ADPODS and 2 wt% Span 80. With increasing salinity, these two systems transform from Winsor type I to III to II as is typical of anionic surfactant-based systems. The microemulsion transition is governed by the hydrophilicity and lipophilicity of the system as described by the Winsor R ratio of interactions (32), which are simplified to include the surfactant, oil and water self – interactions as in Equation 1:

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \qquad [1]$$

where A_{CO} is the interaction (per unit interfacial area) between the surfactant and the oil, A_{CW} is the interaction between the surfactant and the aqueous phase, L and H refer to lipophilic and hydrophilic, and A_{LL} and A_{HH} are self-interaction of the lipophilic and the hydrophilic portions of the surfactant, respectively. The parameters A_{WW} and A_{OO} are self-interaction in the water phase and oil phase, respectively. The numerator of the equation represents the net interaction of the

the optimum formulation corresponds to R values equal to 1, or when the interactions of the lipophilic and hydrophilic regions are in balance. For $R\ll1$, the interface becomes more hydrophilic, and a micellar solution or an O/W microemulsions exists. At $R\gg1$, inverse micelles form and the solution becomes a W/O microemulsion. Salager *et. al* (29) described the relationship of Equation 1 to the solubilization parameters. To enhance the solubilization of both oil and water, the interactions of both the hydrophilic part and lipophilic part of the interface must be increased.

Based on their relative EACN values (16 for hexadecane and 23.5 for motor oil), as expected, the experimental S* value for motor oil (16.0% NaCl) is higher than that for hexadecane (8.0% NaCl) (see Figure 3). From the results, it can be concluded that the higher EACN oil requires higher salinity to form Winsor type III microemulsions and to reach the optimum conditions. This result corresponds to the results that were observed by others (32). Interestingly, Winsor type II microemulsion cannot be observed in the experiment with this surfactant formulation with motor oil due to its high hydrophobicity.

In the system of hexadecane, which is less hydrophobic, the self-interaction of the oil (A_{OO}) is smaller as compared to motor oil. Thus, the overall value of the numerator in Equation 1 increases. To reach the optimum condition at $R = 1$, the denominator of Equation 1 has to increase as well. This can be achieved by reducing the salinity of the system, which will lead to an increase in A_{CW}. Consequently, the optimum salinity of the hexadecane system is lower than that of the motor oil system. In this study, the SP* value of the system with hexadecane was found to be higher than the one of the system with motor oil; 2.69 mL/g and 1.98 mL/g, respectively. The results obtained from this study correspond to the results reported by Bourrel *et al.* (33). It can be concluded that an increase in either salinity or alkane carbon number of the oil results in a decrease in the solubilization parameter. This trend has been also reported for several sulfonate surfactants (28).

Phase behavior with surfactant scan. For the hexadecane system, a mixture of 2% AOT, 2% ADPODS and 2% Span 80 was used as a base condition from which subsequent variations were made. When the system was scanned for either AOT, or ADPODS, or Span 80, the other two surfactant concentrations were kept constant. For instance, the AOT scan was performed at 5% sodium chloride, so the

system mixture contained 2% ADPODS and 2% Span 80 in 5% NaCl, and the scan involved changing only the AOT concentration. Four salt concentrations were used for the systems with hexadecane: 5, 7.5, 10 and 12.5% NaCl. The motor oil systems had base concentrations of 3% AOT, 2% ADPODS, and 2% Span 80. The electrolyte concentrations for the motor oil system were 5.0, 10.0, 15.0 and 20.0% NaCl.

Winsor type I to type III and to type II transitions were observed in the systems with four concentrations of NaCl (5, 7.5, 10 and 12.5%) as AOT concentration was varied for the hexadecane system (Figure 4a). The higher the concentration of sodium chloride, the lower the weight fraction of AOT needed for the phase transition from type I to type III. Similar results appear for the Span 80 scan system. Increasing electrolyte concentration tends to decrease surfactant water solubility. To maintain the system at the optimum when salt concentration in the system increases, the lipophilicity at the interface has to be decreased. Consequently, both weight fractions of AOT and Span 80 at the optimum were decreased at a higher salinity. However, because of higher hydrophobicity, the weight fraction of Span 80 required for type I-III phase transition was less than that of AOT. Conversely, the ADPODS scan system shows the opposite transition, from type II to type III and then type I, due to the very high hydrophilicity of ADPODS. Consequently, an increase in ADPODS fraction of the system results in an increase in the hydrophilicity of the system. Table 2 summarizes the phase transition of the studied systems with hexadecane.

For the motor oil system, the AOT scan at four concentrations of NaCl (5, 10, 15 and 20%) exhibited the Winsor type I to III transition, but the type III to II transition was not observed up to AOT wt. fraction as high as 0.8 (Figure. 4b). This is because the increase in AOT actually affects the interaction on both sides of the interface, as it is an anionic and lipophilic surfactant. Nonetheless, in the system with high EACN oil like motor oil, the interaction of the lipophilic part of the surfactant is not high enough to overcome the interaction of the hydrophilic part of the surfactant to generate inverse micellar microemulsions (type II). For the Span 80 scan system at low salinity (5% NaCl), the system behaved in the same way as in the case of the AOT scan in that only the transition from type I to III was observed. On

the other hand, when the salinity increased to 10% and higher, a type I microemulsion was not observed because the higher salinity reduced hydrophilicity of the system. The middle phase appeared even without Span 80; however at higher salt concentrations (15 and 20% NaCl), the transition from type III to II occurred. From the results of the Span 80 scan, it can be implied that at 10 % NaCl and higher, the system of 3% AOT and 2% ADPODS can produce middle phase microemulsion formation with motor oil. Accordingly, in the system of variable surfactant scan with motor oil, only the systems with the ADPODS scan shows the 3 types of microemulsions and the transition is from type II-III-I. Table 3 summaries the phase transitions of surfactant scans with motor oil.

It can be concluded experimentally that single surfactants are not generally able to form microemulsions with some types of oils, especially highly hydrophobic oils. Hence, the application of mixed surfactants becomes necessary for microemulsion formation. In the case where there is a large difference in HLB of a two-surfactant mixture, a third component should be introduced. This confirms our hypothesis that a mixed surfactant system inspired by the linker concept (34) has the capacity to bridge the wide HLB gap between water and hydrophobic oils. From our mixed surfactant systems, a change in lipophilic surfactant fraction ratio leads to the same result as a change in salinity.

Solubilization of hexadecane and motor oil in mixed surfactants. The Winsor's R-ratio in Equation 1 clearly explains the observed trends in terms of interaction energies. According to the Winsor's concept, the greater the cohesive energy between the amphiphile at the interfacial layer both in the oil and in the water regions, the higher the solvency of the system. Thus, to increase solubilization, in Equation 1 both the numerator or the net interaction of the lipophilic portion (A_{CO} - A_{OO} -A_{LL}) and the denominator or the net interaction energy of the hydrophilic portion (A_{CW} -A_{WW} -A_{HH}) have to be increased. As a consequence, the system with higher salinity that reduces cohesive energies in the water region (A_{CW}) thereby reduces the SP* of the system (32). The results of the AOT, ADPODS and Span 80 scan systems at various concentrations of salt agree with this explanation. Figures 5(a) and 5(b) show the correlation between SP* and NaCl concentrations for each scan of the systems with hexadecane and motor oil, respectively. The change in

salinity is likely to have much less influence on SP* in the AOT scan systems for both oils than in ADPODS and Span 80 scans. This is due to the fact that AOT is a surfactant with nearly balanced hydrophilic and lipophilic portions (2). Therefore, the increased weight fraction of AOT has equal influence on both sides of the interface. Subsequently, the SP* of the system in the AOT scan was less affected by the increasing salinity compared to the ADPODS and Span 80 scans, which are highly hydrophilic and lipophilic, respectively.

IFT at optimum and supersolubilization region. Interfacial tension (IFT) between oil and water is related to free energy difference of the interfacial film at the planar interface separating the bulk phases and at the curved interface of the microemulsion droplet. The microstructure of the middle phase is considered to be bicontinuous (35) and as a consequence, its curvature is almost planar. Therefore the difference in free energy is very low, resulting in an ultralow IFT. The results show ultralow values of IFT*, which are in the range of 10^{-2} to 10^{-3} mN/m as compared to the relatively low values of IFT in the supersolubilization region, which are in the range of 10^{-1} to 10^{-3} mN/m (see Figure 6 and Figure 7). The IFT values in the supersolubilization region are considered to be in the useful range for detergency applications (36).

The IFT increases with salinity for both hexadecane and motor oil systems as shown in Figure 8, which, as will be explained in the next section, is due to the decrease of SP* with increased salinity, as discussed before. As a consequence, the AOT and ADPODS scans exhibited a monotonic increase in IFT with an increase in the salinity of the systems.

Correlation between IFT and SP. Huh (37,38) related the solubilization parameter (SP) and interfacial tension (IFT) in the well known Chun-Huh equation as shown in Equation 2 (where C is a constant).

$$SP^2 * IFT = C \qquad [2]$$

The model relates all energy terms to microemulsion interface curvature and explains the relation of SP or the thickness of the interface to the interfacial curvature. The work of Huh (37) involved the analysis of the molecular interactions between alternative flat layers of oil and water present in the middle phase microemulsion.

The original equation uses the thickness of the layers of oil and water instead of the solubilization parameter, but since the thickness comes from the ratio of volume of the oil (or water), divided by the interfacial area provided by the adsorption of the surfactant at the interface, it has been simplified to the ratio of volume to the volume or mass of the surfactant. Subsequently, Pope and Wade (39) reported that Equation 2 also represents microemulsion results for several chlorinated organics (e.g., trichloroethylene and perchloroethylene), with the C in Equation 2 also being around 0.3. These chlorinated organics generally have very low EACN values, even negative in some cases. Figure 9 shows the plot of IFT versus SP for the systems with the motor oil and hexadecane at optimum condition and in the supersolubilization region with the best fit of Equation 2. The Chun-Huh equation fits the data for both hexadecane and motor oil extremely well with C = 0.04. The disparity between the C value obtained in this work and the value reported in the literature is explained by the definition of the solubilization parameter. In the literature, medium chain alcohols are used as cosurfactants but are not taken into account in the calculation of SP. Since this work uses alcohol-free systems and we consider all the surfactants in the calculation of SP, our SP values are lower compared to those reported in the literature, and therefore a lower C value results.

In addition, the hexadecane and motor oil may have a lower extent of penetration into micellar solution due to their larger size. This can be seen from low SP of hexadecane and motor oil as compared to those of lower EACN oil like decane or heptane. For example, for hexadecane (EACN =16) the highest solubilization parameter is around 4.5 mL hexadecane per g surfactant, while Pope and Wade (39) presented results for decane (EACN =10) showing that the highest SP value was almost 15 mL decane per g surfactant (traditionally surfactant is expressed as a volume, but a density of 1 g/mL is usually assumed, so the units are the same, de facto). It is also interesting (and fortuitous) that the same universal relationship holds for a given oil for both type I (at supersolubilization) and type III systems. This permits estimation of IFT from the more easily measured SP values. Aarra *et al.* (40) showed the estimation of IFT* value by the Chun-Huh equation for systems of sodium dodecyl sulfate with heptane from SP* value and C equal 0.3 and found that the IFT* value were in the range of ultralow (10^{-3} mN/m) as expected.

More recent efforts have extended the early Chun-Huh approach by considering the characteristic length, or the extent to which the surfactant impacts the oil phase (41,42). This new approach helps to overcome some of the issues we have discussed relative to the way the Chun-Huh relationship has been used. However, a detailed discussion of this new approach is beyond the scope of this paper, and we have chosen to reference the Chun-Huh approach since this has been commonly used in the literature

Temperature effect. Since an increase in temperature has opposing effects on phase transitions for nonionic and ionic surfactants, the temperature dependence of phase change of the mixed nonionic and ionic surfactant system depends upon the type and ratio of the surfactants. In this study, the SP* and S* were obtained from salinity scans of a system composed of 3% AOT, 2% ADPODS and 2% Span 80 at different temperatures. The results shown in Figure 10 indicate that an increase in temperature leads to increasing optimum salinity (S*). These results reveal that our mixed surfactant system behaves qualitatively as an ionic surfactant system in that a higher temperature causes the HLB of the interface to increase (type II to III to I transition). It is not surprising that for any given temperature, the S* value of hexadecane is much less than that of motor oil as shown in Figure 11. On the other hand, for any given temperature, the SP* of the system with hexadecane is significantly higher than that with motor oil (see also Figure 11). For this formulation, the overall system is influenced by the ionic surfactants, thus the hydrophilicity is increased when temperature increases. Consequently, higher salinity decreases HLB while an increase in temperature increases HLB. Thus a higher optimum salinity appears at a higher temperature. Nonetheless, the microemulsion formation from this formulation of surfactant mixture with hexadecane and motor oil can be considered as temperature insensitive microemulsions, especially in the range of 20-40 °C because S* increased by less than 0.1% per °C for both hexadecane and the motor oil. These systems are robust with respect to temperature, which is very beneficial for detergency application.

General observations related to detergency. In part II of this series, we will relate microemulsion phase behavior to oily soil detergency experimental results.

But, some important conclusions from this works which relate to detergency can be noted.

1. Mixtures of surfactants with widely varying HLB values can achieve Winsor type III microemulsions which are temperature-robust.

2. SP and IFT values under supersolubilization conditions (i.e, in a type I system) are not substantially worse than under optimum conditions in a type III system. In other words, quite low interfacial tensions can be attained without formation of a middle phase.

3. For the systems studied, the salinity required to attain supersolubilization conditions or optimum conditions is fairly high (ca. 5% NaCl). However, given the desirable characteristics of these systems, the formulation can be modified to achieve lower salinity systems.

4. The solubilization (SP) and interfacial tension (IFT) data follow the trend predicted by the simplified Chun-Huh equation. The microemulsion systems formulated can achieve ultralow interfacial tension and modest solubilization of very hydrophobic oils (motor oil and hexadecane)

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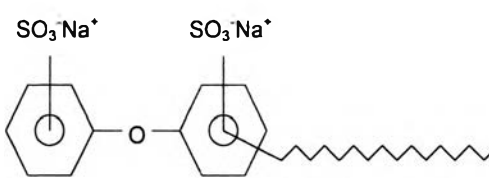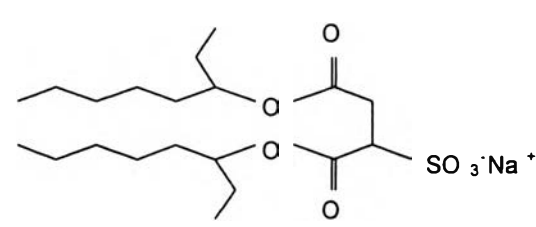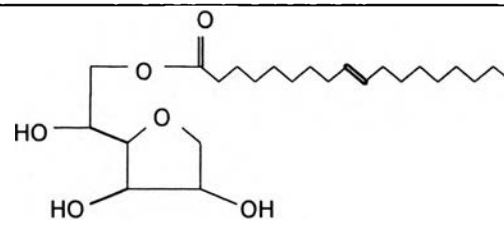
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TABLE 1

Properties of Surfactants Used in the Study

Chemical Name	Chemical Formula/Structure	MW	HLB
Alkyl diphenyl oxide disulfonate, ADPODS (Dowfax 8390)	$SO_3^-Na^+$ $SO_3^-Na^+$	642	> 40*
Bis (2-ethylhexyl) sulfosuccinic acid sodium salt (AOT) (dioctyl sulfosuccinate)	$SO_3^-Na^+$	444	10.2**
Sorbitan monooleate (Span 80)		428.6	4.3

Note   * For Dowfax 8390, the HLB is not available, however, it is reported that its HLB is higher than   sodium dodecyl benzene sulfonate whose HLB is around 40. (24)

   * *   HLB value in a 1% brine (23)

TABLE 2

Summary of Phase Transition of the Mixed Surfactants Systems with Hexadecane

*1) 2 % ADPODS, 2 % Span 80 and AOT at various salt concentrations:*

NaCl concentration (%)	Range of AOT (wt. fraction)	Range of middle phase (wt. fraction of AOT)	Observed phase transition
5.0	0.200-0.789	0.556-0.692	Type I to III to II
7.5	0.200-0.789	0.500-0.652	Type I to III to II
10.0	0.111-0.667	0.335-0.556	Type I to III to II
12.5	0.111-0.667	0.273-0.429	Type I to III to II

2) 2% AOT, 2% Span 80 and ADPODS at various salt concentrations:

NaCl concentration (%)	Range of ADPODS (wt. fraction)	Range of middle phase (wt. fraction of ADPODS)	Observed phase transition
5.0	0.059-0.333	0.200-0.238	Type II to III to I
7.5	0.059-0.556	0.216-0.273	Type II to III to I
10.0	0.000-0.556	0.304-0.385	Type II to III to I
12.5	0.000-0.600	0.273-0.385	Type II to III to I

3) 2% AOT, 2% ADPODS and Span 80 at various salt concentrations:

NaCl concentration (%)	Range of Span 80 (wt. fraction)	Range of middle phase (wt. fraction of Span 80)	Observed phase transition
5.0	0.333-0.600	0.490-0.515	Type I to III to II
7.5	0.200-0.636	0.385-0.467	Type I to III to II
10.0	0.000-0.636	0.333-0.429	Type I to III to II
12.5	0.000-0.556	0.273-0.385	Type I to III to II

Table 3

Summary of Phase Transition of the Mixed Surfactants Systems with Motor Oil

1) 2% ADPODS, 2% Span 80 and AOT at various salt concentrations:

NaCl concentration (%)	Range of AOT (wt. fraction)	Range of middle phase (wt. fraction of AOT)	Observed phase transition
5.0	0.000-0.765	0.500-0.765	Type I to III
10.0	0.000-0.789	0.422-0.789	Type I to III
15.0	0.000-0.789	0.273-0.789	Type I to III
20.0	0.000-0.789	0.200-0.789	Type I to III

2) 3% AOT, 2% Span 80 and ADPODS at various salt concentrations:

NaCl concentration (%)	Range of ADPODS (wt. fraction)	Range of middle phase (wt. fraction of ADPODS)	Observed phase transition
5.0	0.000-0.375	0.167-0.231	Type II to III to I
10.0	0.000-0.375	0.167-0.259	Type II to III to I
15.0	0.000-0.667	0.167-0.333	Type II to III and then precipitate after type III
20.0	0.000-0.645	0.167-0.412	Type II to III and then precipitate after type III

3) 3% AOT, 2% ADPODS and Span 80 at various salt concentrations:

NaCl concentration (%)	Range of Span 80 (wt. fraction)	Range of middle phase (wt. fraction of Span 80)	Observed phase transition
5.0	0.091-0.706	0.474-0.706	Type I to III
10.0	0.000-0.706	0.167-0.706	Only type III
15.0	0.000-0.706	0.000-0.583	Type III to II
20.0	0.000-0.706	0.000-0.500	Type III to II
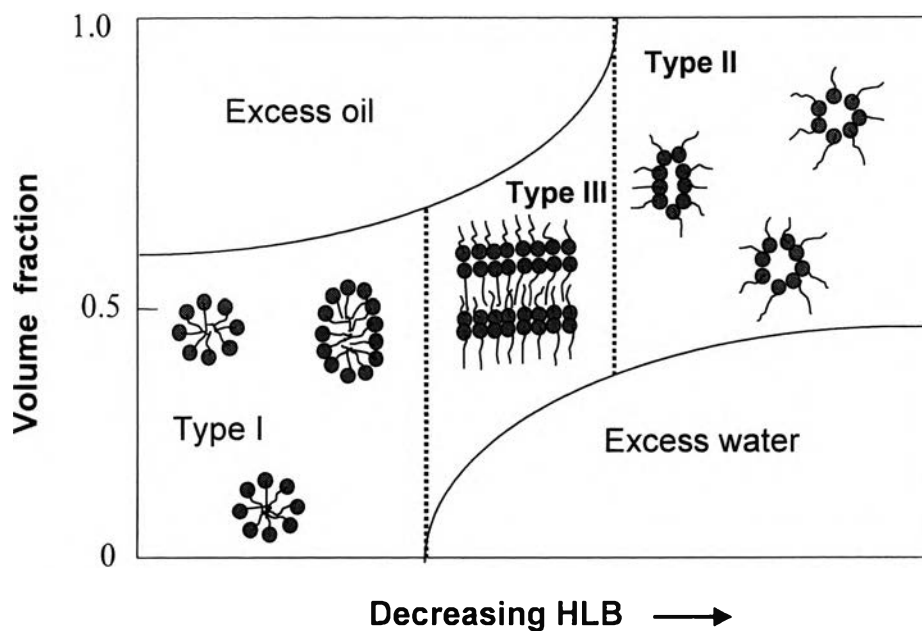
FIG. 1 Typical phase behavior showing the transition from oil in water (type I) to bicontinuous structure (Type III) and water in oil structure (type II); initial volume ratio of oil to water = 1:1.
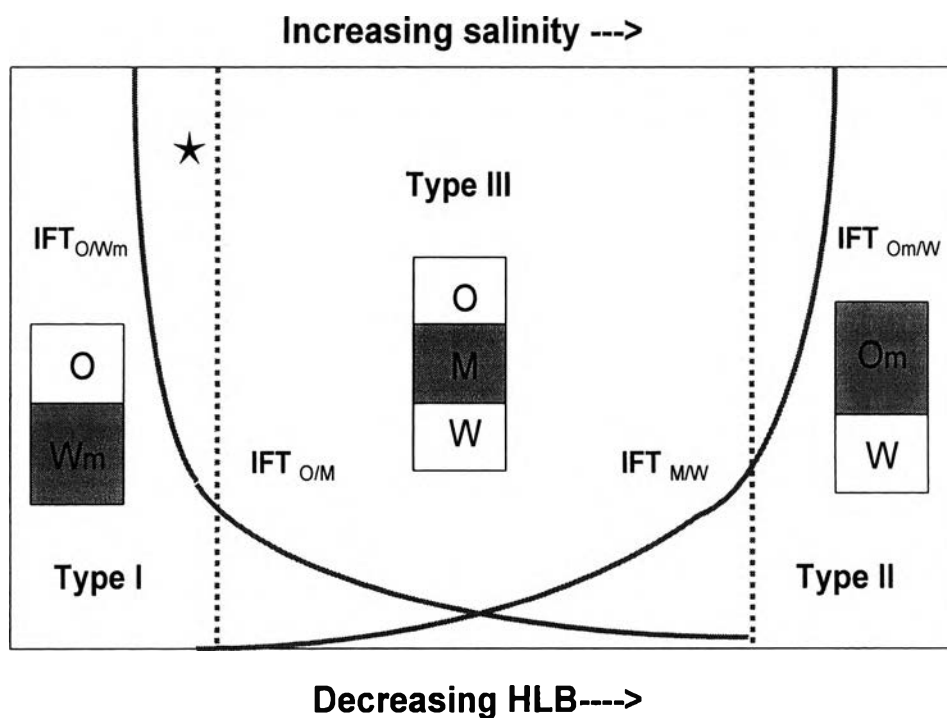

FIG. 2 Phase behavior showing interfacial tension (IFT) as a function of scanning variables. Where O is oil; W is water; M is middle phase; Wm is O/W microemulsion; Om is W/O microemulsion; and ★ is supersolubilization region.
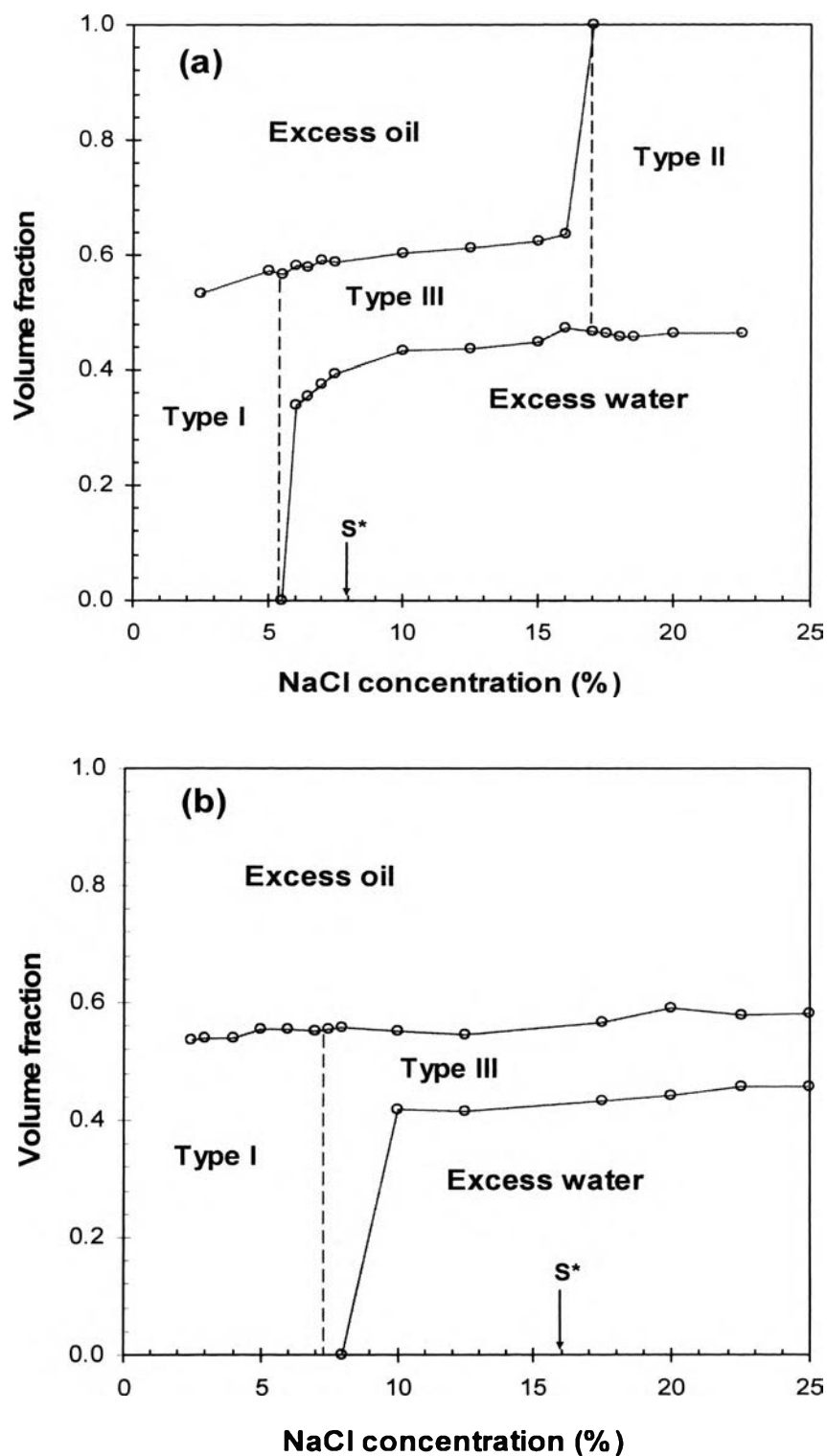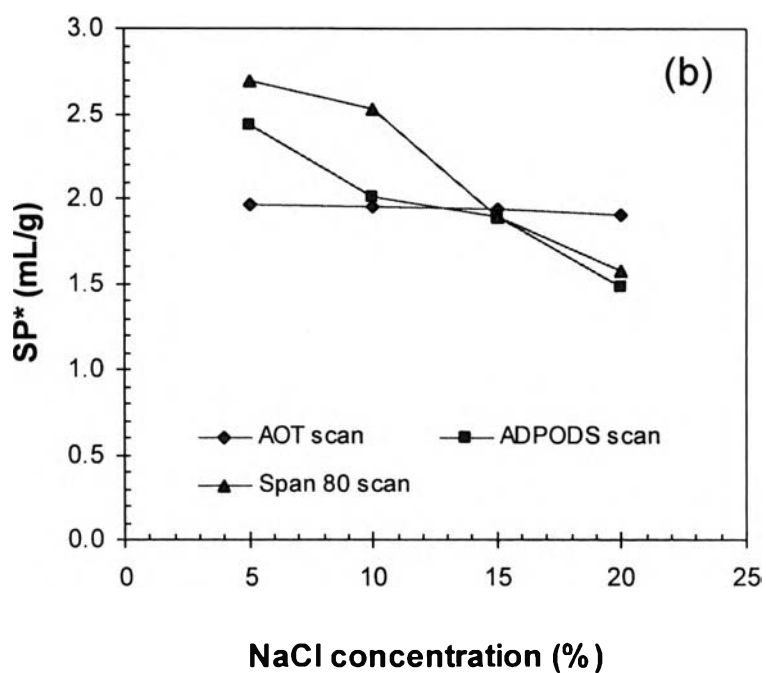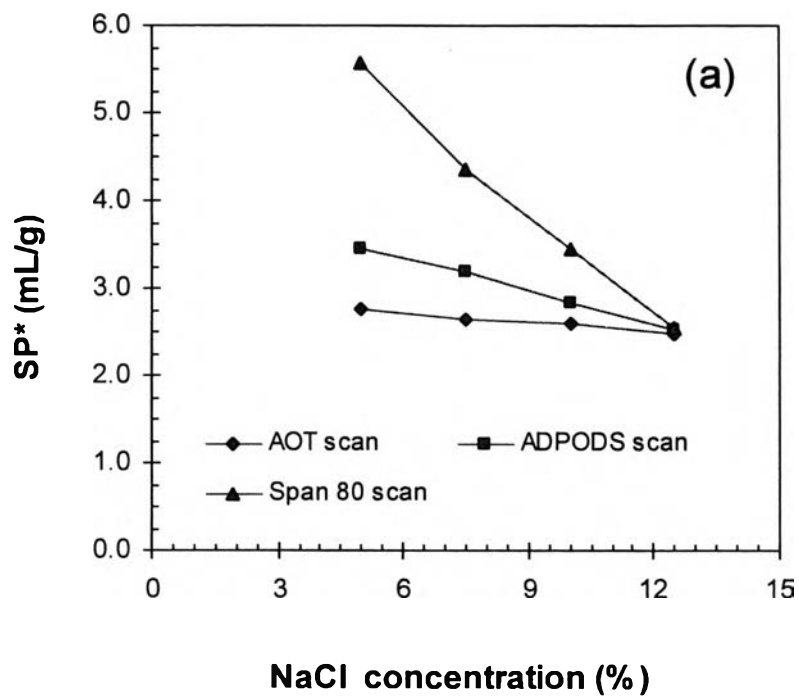
FIG. 3 Phase diagram of the system of 3% AOT, 2% ADPODS and 2% Span 80 with salinity scan for (a) hexadecane and (b) motor oil; initial volume ratio oil to water = 1:1, and S* is optimum salinity.
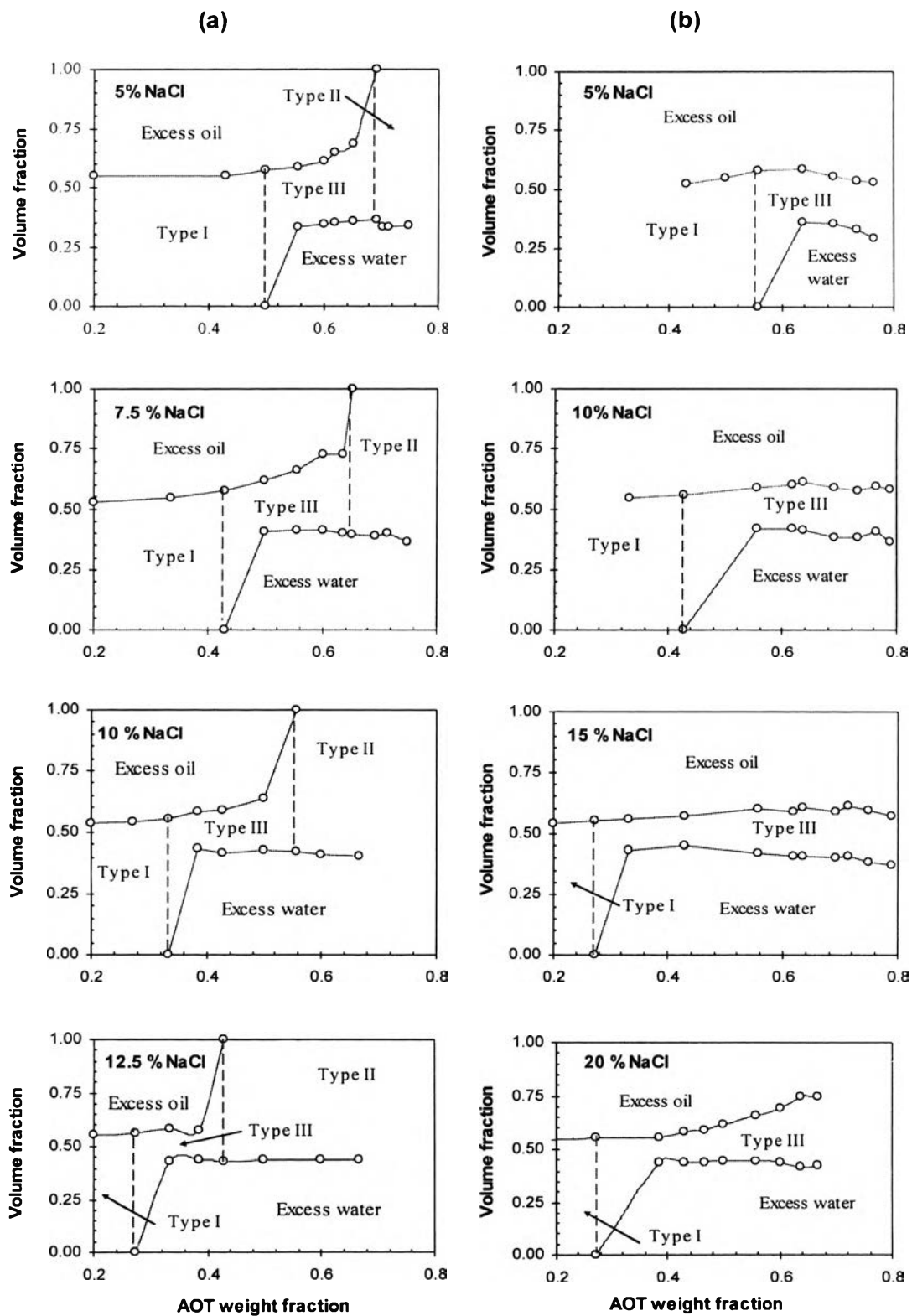
FIG. 4 Phase behavior of the system with AOT Scan, 2 % ADPODS and 2 % Span 80 with (a) hexadecane and (b) motor oil at 25 °C

FIG. 5 SP* as a function of salinity of mixed surfactant systems of AOT, ADPODS and Span 80 at 25 °C with (a) hexadecane and (b) motor oil.
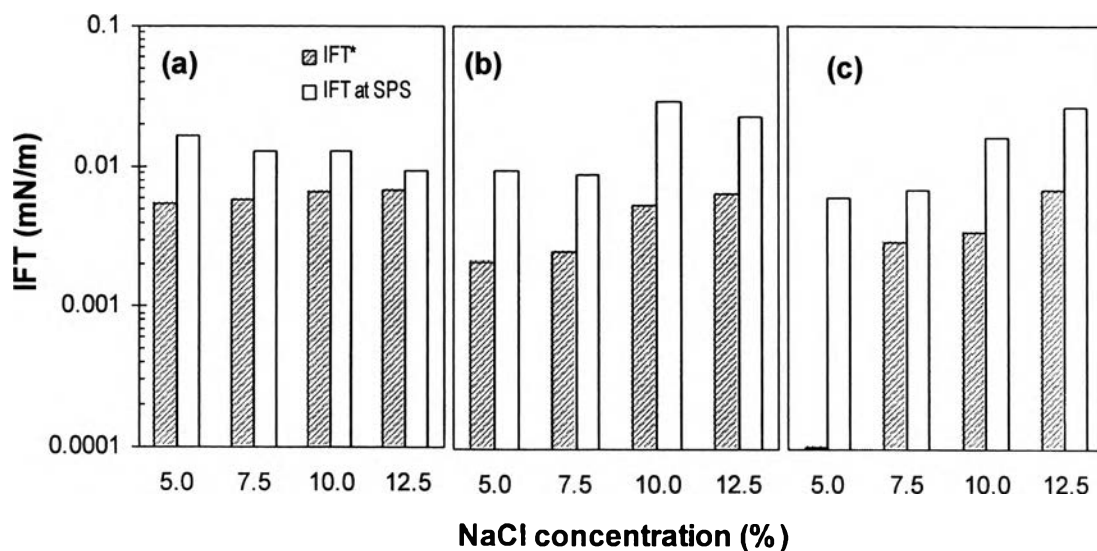
FIG. 6 IFT at optimum condition (IFT*) in the middle phase and at supersolubilization (SPS) with hexadecane at different salt concentration (a) AOT scan system; (b) ADPODS scan system; and (c) Span 80 scan system.
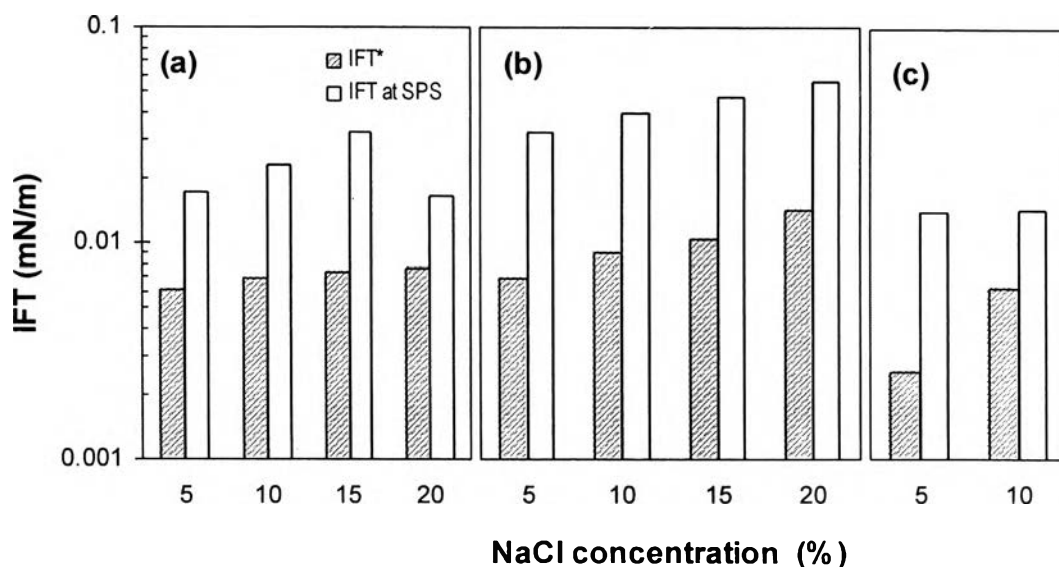

FIG. 7 IFT at optimum condition (IFT*) in the middle phase and at supersolubilization (SPS) with motor oil at different salt concentration (a) AOT scan system; (b) ADPODS scan system; and (c) Span 80 scan system.

(a)

(b)
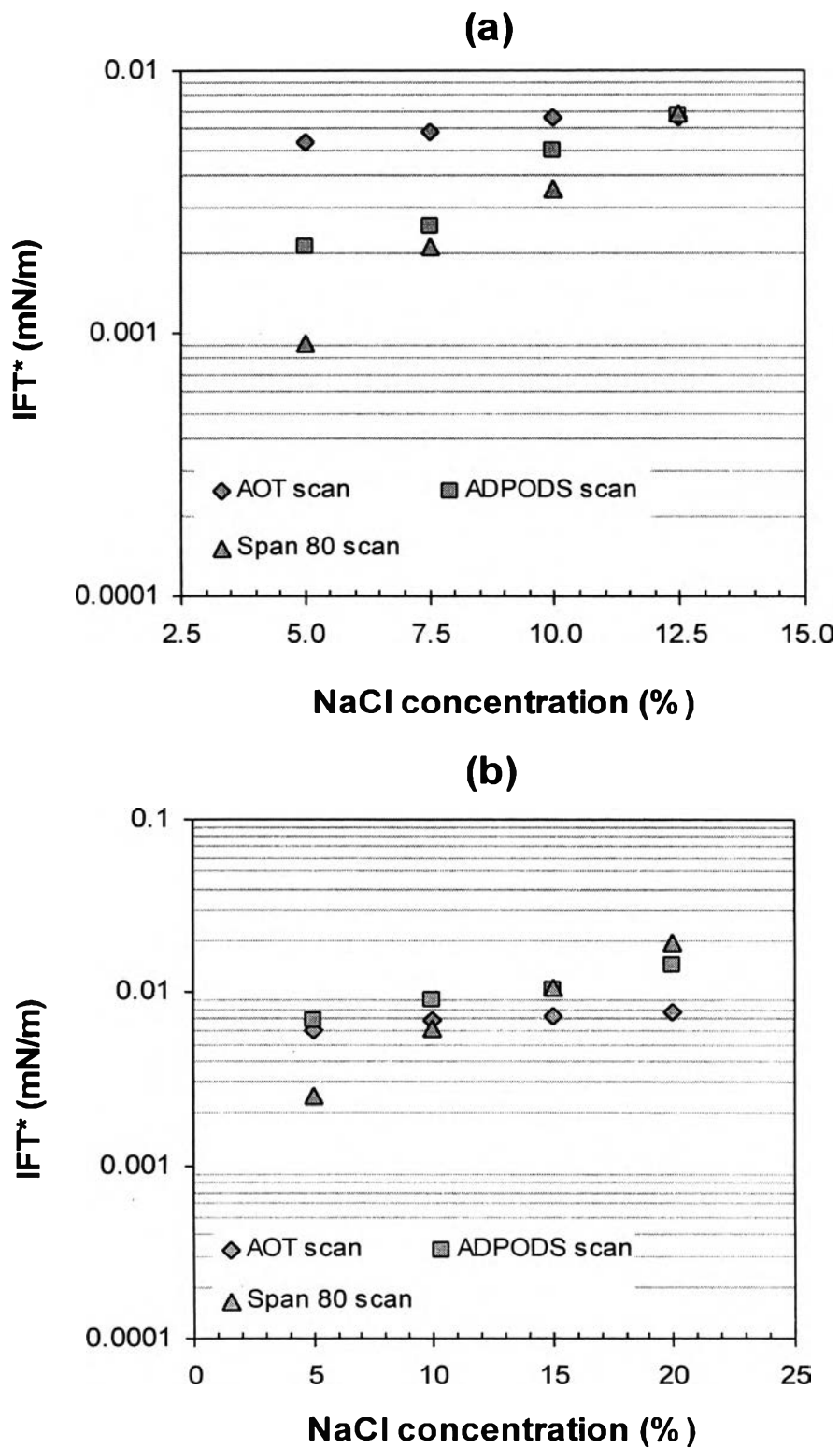
FIG. 8 The interfacial tension at optimum (IFT*) of the mixed surfactants systems of AOT, ADPODS and Span 80 with (a) hexadecane and (b) motor oil.
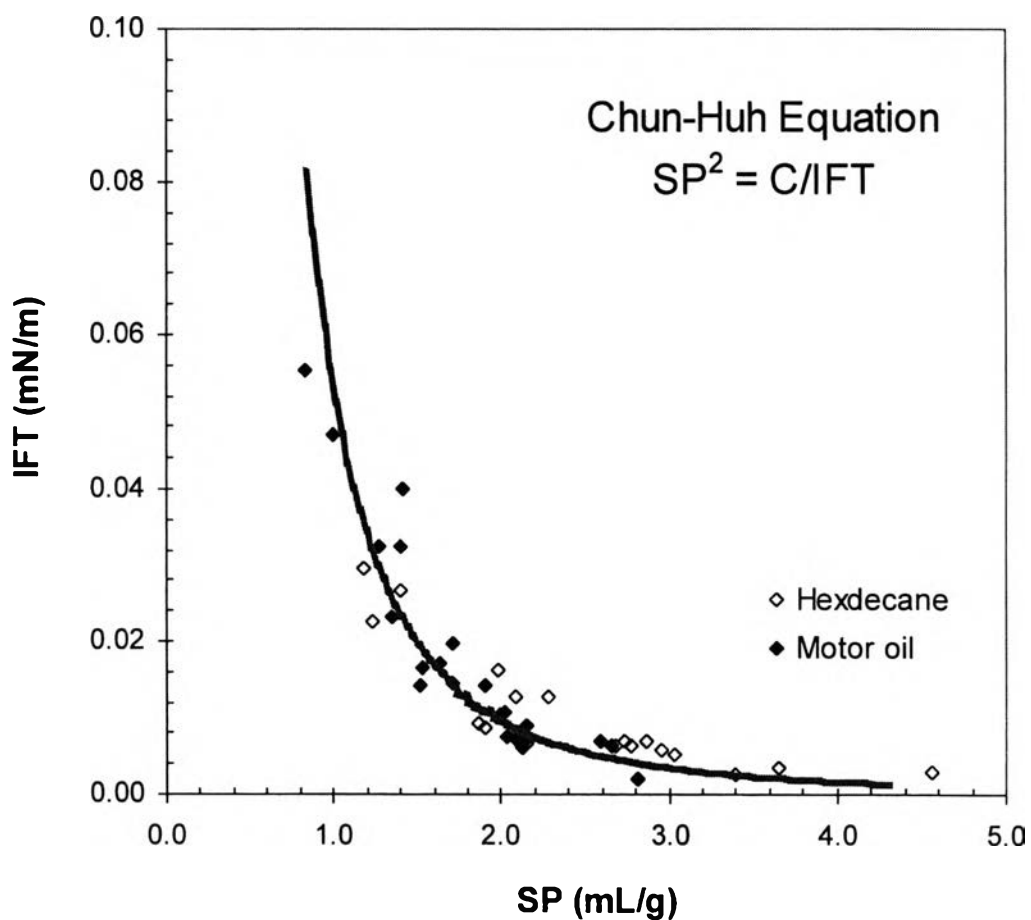
FIG. 9 Relation of solubilization parameter (SP) and interfacial tension (IFT) at optimum and at supersolubilization of the systems of AOT/ADPOD /Span 80/ electrolyte and oils (hexadecane and motor oil).
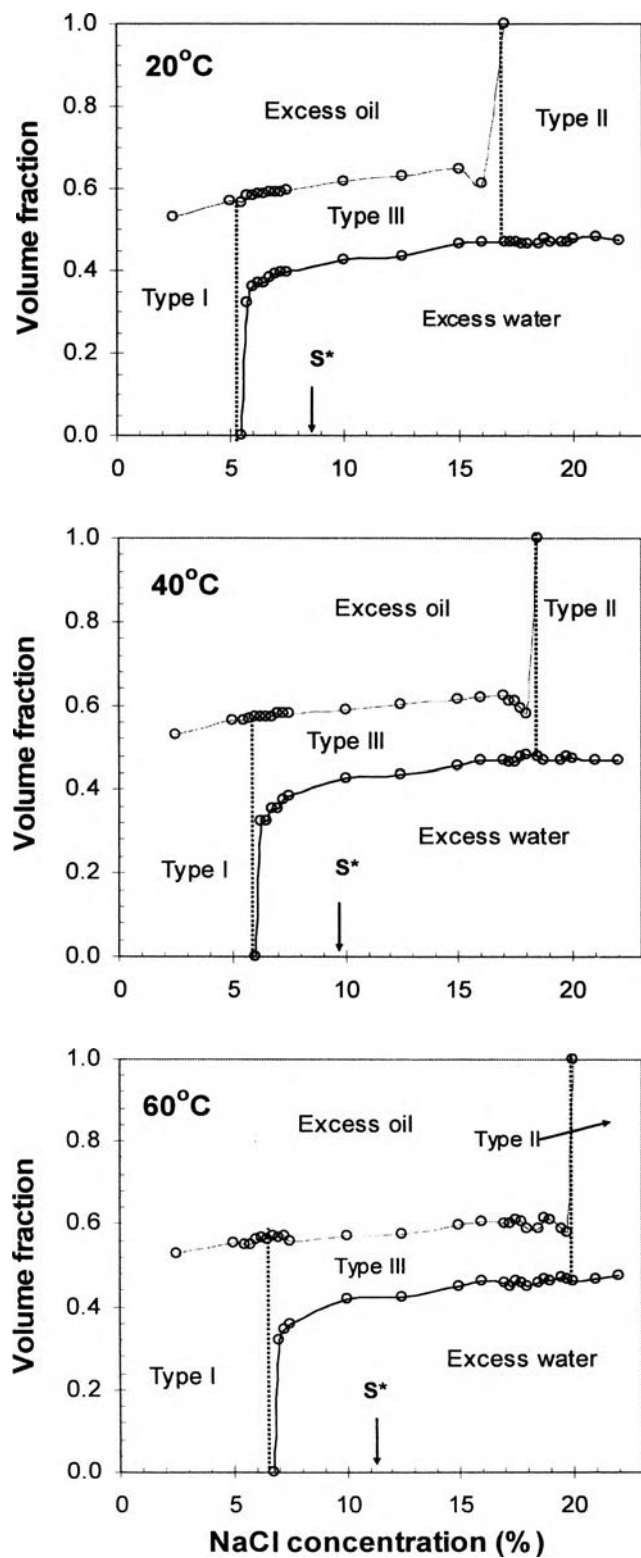
FIG. 10 Phase diagram of the system of 3% AOT, 2% ADPODS, 2% Span 80 and salinity scan with hexadecane at different temperatures; initial volume ratio of oil to water = 1:1.
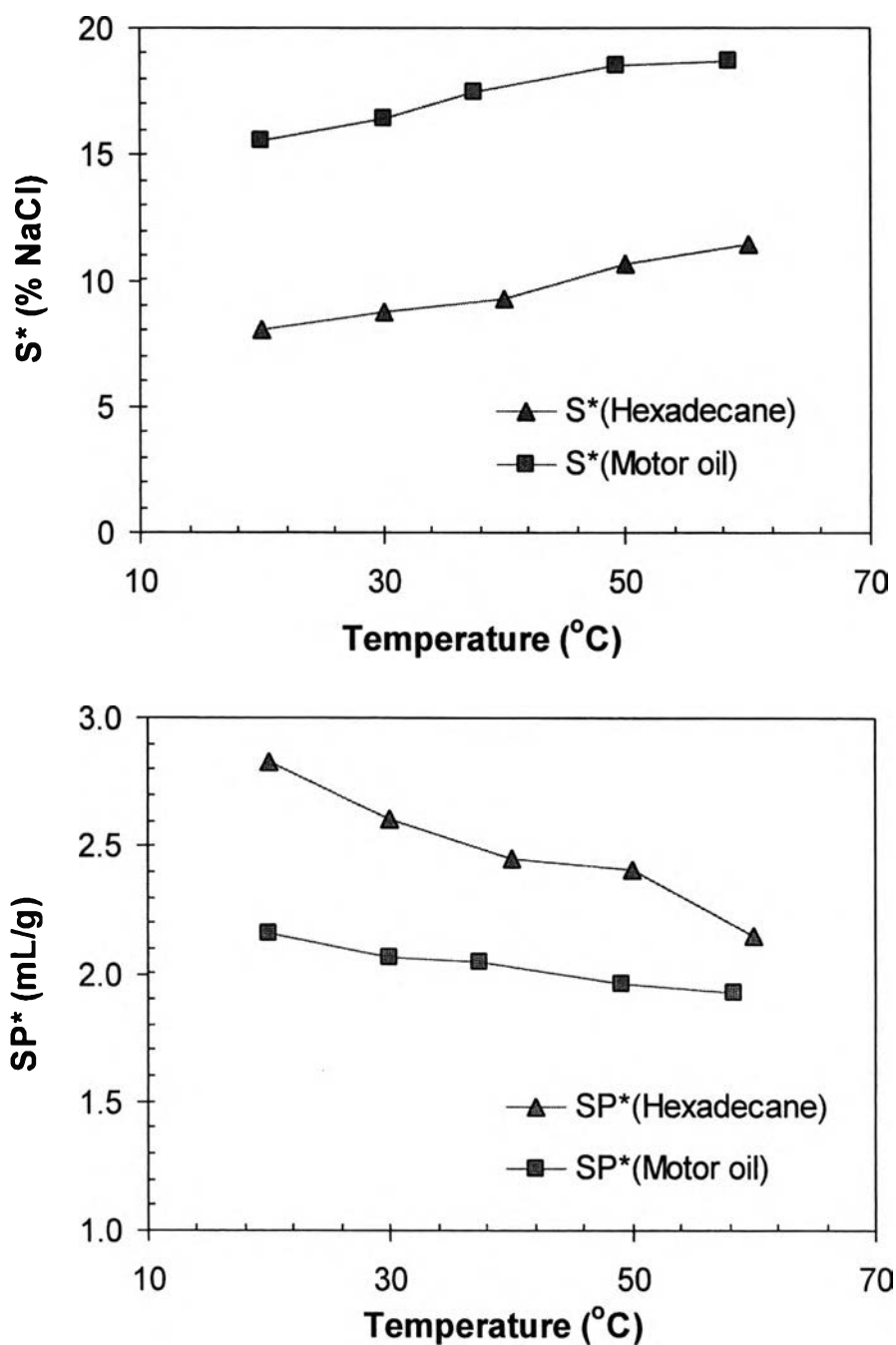
FIG.11 Optimum salinity (S*) and optimum solubilization parameter (SP*) as a function of temperature of the system 3% AOT, 2% ADPODS, and 2% Span 80