The Role of Hydrophilic Linkers

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ABSTRACT: In microemulsion formulations, linker molecules are additives that can enhance the surfactant–oil interaction (lipophilic linkers) or the surfactant–water interaction (hydrophilic linkers). In this paper, the role of the hydrophilic linker is elucidated through solubilization studies, interfacial tension studies, and by studying the partitioning of the hydrophilic linker into an optimum middle phase. This research used alkyl naphthalene sulfonates as the hydrophilic linkers, sodium dihexyl sulfosuccinate as the surfactant, and trichloroethylene as the oil phase. The hydrophilic linkers were found to have interfacial properties between a hydrotrope and a cosurfactant. More specifically, the data show that a hydrophilic linker is an amphiphile that coadsorbs with the surfactant at the oil/water interface but that has negligible interaction with the oil phase. The role of the hydrophilic linker can thus be interpreted as opening "holes" in the interface. Based on the characteristics of alkyl naphthalene linkers, carboxylic molecules were evaluated as hydrophilic linkers. For trichloroethylene microemulsions, sodium octanoate was found to be an alternative hydrophilic linker to sodium mono- and dimethyl naphthalene sulfonates.

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KEY WORDS: Hydrophilic, hydrotrope, linker, microemulsion, octanoate, trichloroethylene.

Microemulsions are thermodynamically stable isotropic emulsions with nanometer-sized aggregates (1,2). A microemulsion can be oil solubilized in water (Winsor Type I), water in oil (Type II), or bicontinuously in oil and water (Winsor Type III middle phase). Microemulsions are characterized by ultralow interfacial tensions and a high capacity to dissolve oil and water into single clear phases. The transitions among the different types of microemulsions can be achieved under certain formulation conditions that change the hydrophilic/lipophilic balance (HLB) of the surfactant at the oil/water interface. More detailed descriptions of microemulsion systems can be found elsewhere (1–4).

Figure 1 shows an example of the Winsor phase transitions discussed above, where salinity is used to produce the phase transition. By increasing salinity, the microemulsion phase changes from Type I to Type III (middle phase) to Type II. The point at which the same amount of oil and water are solubilized in Type III is known as the optimum formulation. At the optimum formulation, the interfacial tension between the excess oil and water reaches a minimal value. The solubilization and formulation results presented later will be for such optimum conditions.

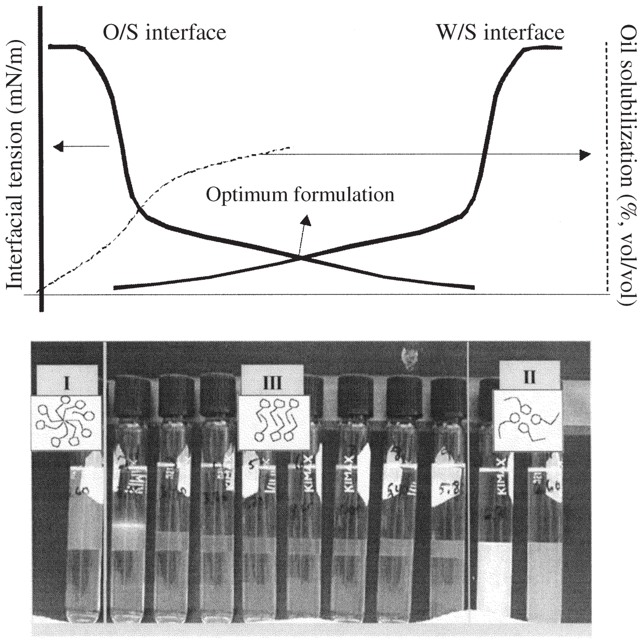

FIG. 1. Typical surfactant phase behavior for a dense chlorinated hydrocarbon showing the transition from Winsor Type I → III → II with corresponding interfacial tension and solubilization level. Phase changes occur with an increase in salinity, a decrease in temperature, or an increase in long-chain alcohol content. O, oil; S, surfactant; W, water.

Microemulsion formulations often use additives such as hydrotropes, cosurfactants, cosolvents, and electrolytes to affect the HLB of the amphiphile at the interface. The spectrum of additives can range from very hydrophobic to very hydrophilic. Figure 2 illustrates the relative hydrophilic/lipophilic character of different types of additives relative to their location at the oil/water interface.

Graciaa *et al.* (5,6) introduced the lipophilic linker effect to characterize the role of long-chain alcohols in surfactant formulations. This concept also applies to ethoxylated nonionic surfactants with a low degree of ethoxylation. Lipophilic

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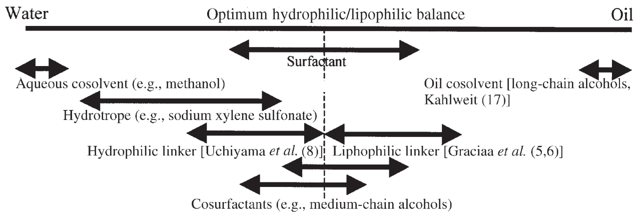


FIG. 2. Relative hydrophilic/lipophilic character of microemulsion additives.

linkers are polar hydrocarbon molecules that adsorb at the palisade layer of the interface, extending the surfactant effect into the oil phase and increasing the surfactant–oil interaction. More recently Salager *et al.* (7) found that the lipophilic linker effect is diminished at a high alcohol-to-surfactant ratio.

Graciaa *et al.* (5,6) and Salager *et al.* (7) used lipophilic linkers to increase the solubilization capacity of isooctane in nonionic surfactant formulations. Uchiyama *et al.* (8) used dodecanol and oleyl alcohol as lipophilic linker molecules in microemulsions of chlorinated hydrocarbons using the anionic surfactant sodium dihexyl sulfosuccinate. For chlorinated hydrocarbons, the lipophilic linker also showed a limited capacity to increase the solubility of this system.

Uchiyama *et al.* (8) proposed the hydrophilic linker as a way to complement the lipophilic linker effect and further enhance solubilization results. They used sodium mono- and dimethyl naphthalene sulfonate (SMDNS) as the hydrophilic linker based on its previous use by Shiau *et al.* (9) in trichloroethylene (TCE) microemulsions with sodium bis(2-ethyl hexyl) sulfosuccinate.

Alkyl naphthalene sulfonates are generally considered to be hydrotropes (10,11). Hydrotropes are amphiphile molecules with a short lipophilic moiety that can improve the aqueous solubility of lipophiles and reduce the viscosity and cloudiness of an aqueous solution containing a sparing amount of soluble components (10–12).

When considering a homologous series of amphiphiles, the transition from hydrotrope to surfactant behavior is accompanied by distinctive properties (13–16). The hypothesis used in this work is that these special characteristics correspond to the hydrophilic linker effect observed for SMDNS.

Some authors describe the linker effect as a cosolvent effect (17). We will investigate the linker effect using the framework of Graciaa *et al.* (5,6) and Salager *et al.* (7).

The goal of this study is to characterize the role of hydrophilic linkers in optimum microemulsion formulations, as reflected in the optimum salinity, interfacial tension, and synergism with lipophilic linkers. Using these characteristics, additional hydrophilic linkers will be proposed and tested.

EXPERIMENTAL PROCEDURES

Materials. The following chemicals were supplied by Aldrich (Milwaukee, WI) at the concentrations shown in parentheses and used without further purification: TCE > 99%, *n*-dodecanol (>98%), 2-naphthalene sulfonic acid sodium salt (SNS, 90%), sodium chloride (>99%), abietic acid sodium salt (70%), hexanoic acid (98%), heptanoic acid (98%), octanoic acid (98%), and sodium hydroxide (99%). An 80% solution of sodium dihexyl sulfosuccinate (Aerosol-MA®, AMA) that contained less than 5% isopropanol was purchased from Cytec (West Paterson, NJ). SMDNS (Morwet M®) and sodium dibutyl naphthalene sulfonate (SDBNS, Morwet DB®) were supplied by CKWitco (Houston, TX).

Methods. Phase behavior studies were performed using equal volumes of aqueous solution and oil (5 mL each). Electrolyte scans were performed by varying the sodium chloride concentration while holding constant the temperature, additive content (alcohols, acids, hydrotropes, etc.), and pressure (1 atm). Test tubes were placed in a water bath at 27°C (300 K), shaken once a day for 3 d, and left to equilibrate for 2 wk. The phase volumes were determined by measuring the levels of each phase in each test tube. The middle phase volume and the surfactant concentration were used to determine the solubilization parameter.

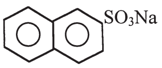
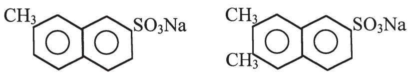
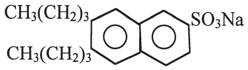
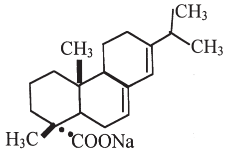
The critical micelle concentration (CMC) of surfactants and hydrotropes was determined by interfacial tension measurements (spinning drop method) using a University of Texas (Austin, TX) spinning drop interfacial tensiometer model 500. For amphiphile/TCE interfacial tension measurements, a 1–5-μL drop of fresh amphiphile solution was injected into a 300-μL sample tube filled with TCE, then spun until equilibrium was achieved (30 min or less). For optimum middle-phase microemulsions, the interfacial tension was measured by injecting 1–5 μL of the middle phase onto a 300-μL tube filled with the excess TCE. All these measurements were performed at 27°C (300 K). Naphthalene sulfonate concentrations were measured using a C8 HPLC column from above, with 80% methanol as the mobile phase, and the detection was performed with a UV Waters (Milford, MA) detector set at a wavelength of 225 nm. Sodium salts of carboxylic acids were obtained by neutralization of the acids with sodium hydroxide.

RESULTS AND DISCUSSION

Solubilization effect of hydrophilic linkers. Uchiyama *et al.* (8) showed that the hydrophilic linker SMDNS has limited capacity to improve the solubilization of chlorinated hydrocarbons. This was attributed to the lack of interaction between SMDNS and the oil. In this research we looked at variations of the SMDNS molecule, namely, sodium naphthalene sulfonate (SNS) and SDBNS. We proposed that these molecules would have properties varying from a hydrotrope to a hydrophilic linker to a cosurfactant, as illustrated in Figure 2. Table 1 shows the chemical structure of these molecules.

Table 2 summarizes the results for the TCE solubilization studies. In the first column of Table 2, “blank” means the optimum formulation for TCE microemulsion using 4% (0.104 M) AMA alone (i.e., no linkers added). Each hy-

TABLE 1
Linkers Studied[a]

Abbreviation	Chemical name	Chemical formula/structure
AMA	Sodium dihexyl sulfosuccinate	$CH_3(CH_2)_5OOCCH(SO_3Na)CH_2COO(CH_2)_5CH_3$
SNS	Sodium naphthalene sulfonate	
SMDNS	Sodium mono- and dimethyl naphthalene sulfonate	
SDBNS	Sodium dibutyl naphthalene sulfonate	
Hexanoate	Sodium hexanoate	$CH_3(CH_2)_4COONa$
Heptanoate	Sodium heptanoate	$CH_3(CH_2)_5COONa$
Octanoate	Sodium octanoate	$CH_3(CH_2)_6COONa$
Abietic acid salt	Abietic acid sodium salt	
Oleate	Sodium oleate	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COONa$
Dodecanol	1-Dodecanol	$CH_3(CH_2)_{11}OH$

[a] Aerosol-MA® (AMA) was purchased from Cytec (West Patterson, NJ). SMDNS and SDBNS were purchased from CK Witco (Houston, TX). SNS was purchased from Aldrich (Milwaukee, WI).

drophilic linker was tested in two types of formulations, alone in a 0.09-M concentration and in combination with dodecanol, a lipophilic linker, at 0.18 M of each additive. The hydrophilic linker alone was expected to have little or no impact on the solubilization capacity, as measured by the solubilization parameter at the optimum formulation (SP*) (8):

$$SP^* = \frac{V_0}{M_s} \qquad [1]$$

where SP* is the solubilization parameter at optimum formulation, V_O is the volume of oil solubilized at optimum, and M_S is the mass of surfactant added.

From Table 2, it can be observed that SNS and SMDNS alone (no dodecanol added) caused no enhancement in the solubilization parameter. For SDBNS formulations, the solubilization parameter increased by 25%, suggesting that SDBNS acts as a cosurfactant rather than a hydrophilic linker in this formulation.

Uchiyama *et al.* (8) observed solubilization enhancement when SMDNS was combined with a lipophilic linker, such as dodecanol. From Table 2, it can be observed that SMDNS and SDBNS showed synergism with dodecanol (i.e., an

TABLE 2
Solubilization Parameters and Fractions of Hydrophilic Linkers (alkyl naphthalene sulfonates) at Optimum Formulations[a]

Hydrophilic linker	Concentration	Dodecanol concentration	Solubilization parameter (mL/g AMA)	Fraction of hydrophilic in Type III (%)	Salinity at optimum (%)
Blank	0	0	5.7 ± 0.7		1.4
SNS	0.09 M	0	5.6 ± 0.7	20	1.5
SNS	0.18 M	0.18 M	5.7 ± 0.7	20	1.7
SMDNS	0.09 M	0	5.4 ± 0.7	50	3.1
SMDNS	0.18 M	0.18 M	10.7 ± 0.7	75	2.8
SDBNS	0.09 M	0	7.1 ± 0.7	69	1.7
SDBNS	0.18 M	0.18 M	14.3 ± 0.7	68	0.7

[a] For abbreviations see Table 1.

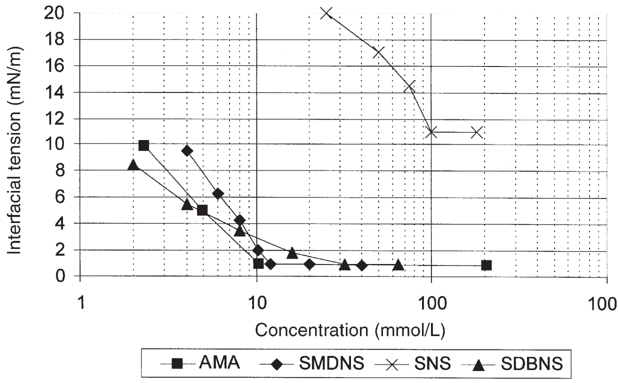


FIG. 3. Interfacial tension of surfactant–trichloroethylene (TCE) systems with varying levels of hydrophile at 300 K. Aerosol-MA® (AMA) was purchased from Cytec (West Patterson, NJ). Sodium mono- and dimethyl naphthalene sulfonate (SMDNS) and sodium dibutyl naphthalene sulfonate (SDBNS) were purchased from CKWitco (Houston, TX). Sodium naphthalene sulfonate (SNS) was purchased from Aldrich (Milwaukee, WI).

increased solubilization parameter), whereas SNS did not. For systems combining either SMDNS or SDBNS with dodecanol, the solubilization parameter was observed to double.

The solubilization studies thus illustrate that whereas the SMDNS acts as a hydrophilic linker, SNS acts as a hydrotrope, and SDBNS acts as a cosurfactant. In order to corroborate this interpretation, the hydrophilic linker concentration was measured in the optimum middle phase by liquid chromatography. This amount was normalized to the total amount added to the formulation, and expressed as "fraction of hydrophilic linker in Type III." Table 2 shows that for SNS the fraction was only 20% and was not increased by the addition of dodecanol. For SMDNS the value was 50% when used alone and was increased to 75% by the addition of dodecanol, evidencing the synergistic effect with lipophilic linkers. When used alone, the SDBNS fraction was the highest, close to 70%, but was not enhanced by the lipophilic linker, which correlates with the hypothesis that it behaves as a cosurfactant rather than as a linker.

To further investigate the hydrophilic linker role and determine why the SNS showed poor incorporation into the middle phase, the interfacial tensions of varying concentrations of each amphiphile vs. TCE were measured at 300 K, and are plotted in Figure 3. The break in the curves in Figure 3 corresponds to the CMC, and the slope is correlated with the Gibbs adsorption isotherm for ionic surfactants and no added salt (18):

$$\Gamma = \frac{-1}{2RT}\left(\frac{d\gamma}{d\ln C}\right) \qquad [2]$$

where Γ is the surface excess concentration of the amphiphile, γ is the interfacial tension, C is the concentration of the amphiphile, R is the gas constant, and T is the absolute temperature of the system.

From the surface excess concentration (Γ, mol/m^2), it is possible to calculate the area per molecule (a, Å^2):

$$a = \frac{10^{20}}{N_A\Gamma} \qquad [3]$$

where N_A is the Avogadro's number and 10^{20} is a conversion factor. Table 3 shows the cmc and area per molecule (a) of the amphiphiles used in this study. It can be noted from Figure 3 that SMDNS, SDBNS, and AMA all have very similar cmc values, which indicates that they can easily coadsorb at the oil/water interface. On the other hand, the SNS cmc is an order of magnitude higher than AMA, which helps explain why SNS accumulates less in the middle phase (i.e., low adsorption at the oil/water interface).

Balasubramanian *et al.* (12) noted that the hydrotrope-to-surfactant transition is related to the apparent cmc of the surface tension curves, and thus the molecule's ability to fit into a micelle. This observation agrees with the values presented in Table 3.

Formulation with hydrophilic linkers. Salager *et al.* (19,20) developed a semiempirical equation to correlate formulation variables based on the change in the chemical potential of the amphiphile:

$$\ln(S^*) = K(\mathrm{ACN}) + f(A) - \sigma + aT\Delta T \qquad [4]$$

where S^* is the salinity at optimum formulation, ACN is the alkane carbon number of the oil phase, $f(A)$ is a function of the surfactant and cosurfactant concentration, σ is the function of alcohol concentration and type, and T is the temperature effect.

Bourrel and Schechter (1) explain the effect of salinity on the phase transition shown in Figure 1. With increased salinity, the electrical double layer around the surfactant head group is compressed, and the electrostatic repulsion decreases. Thus, as the surfactant–water interaction increases, more salinity is required to reach the optimum formulation. Conversely, the greater the surfactant–oil interaction, the lower the salinity necessary to attain the optimum formulation.

Based on this background, hydrophilic linkers should increase the optimum salinity, and lipophilic linkers should decrease it. Figure 4 shows the optimum salinity (S^*) for a 4 wt% (0.104 M) AMA microemulsion as a function of dodecanol (lipophilic linker) concentration, SMDNS (hydrophilic linker) concentration, and a 1:1 mixture of SMDNS and dodecanol at molar concentration. As expected, Figure 4 shows

TABLE 3
Adsorption Characteristics of Amphiphile Molecules[a]

Surfactant	CMC (mMA)	A (Å^2/molecule)
AMA	10 ± 1	120 ± 10
SNS	100 ± 1	60 ± 5
SMDNS	12 ± 1	110 ± 10
SDBNS	20 ± 5	210 ± 20
Sodium heptanoate	1000 ± 10	130 ± 15
Sodium octanoate	45 ± 5	60 ± 5
Abietic acid, sodium salt	5.0 ± 0.5	40 ± 5

[a] For abbreviations see Table 1.

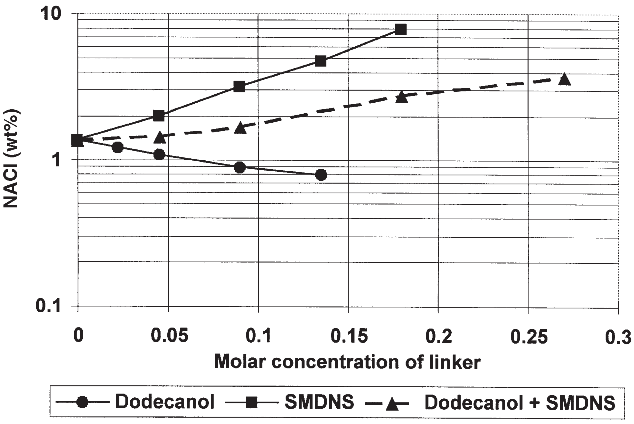


FIG. 4. Salinity at optimum formulation for TCE–AMA (4 wt%) microemulsions with varying levels of hydrophilic (SMDNS), lipophilic (dodecanol), and 1:1 combination of linker molecules. For abbreviations see Figure 3.

that as the hydrophilic linker SMDNS is added, the salinity to achieve the optimum formulation increases proportional to the SMDNS concentration added. Increasing the lipophilic linker (dodecanol) concentration reduces the optimum salinity, and a combination of the two has an intermediate effect.

As can be seen from the above discussion, a hydrophilic linker will tend to increase the salinity at the optimum formulation. The last column in Table 2 shows the optimum salinity for the alkyl naphthalene series. These data demonstrate that, when used alone, SMDNS (0.09 M) has the largest increase in optimum salinity as compared to the blank formulation. Once again, SMDNS is shown to behave most like a hydrophilic linker for the compounds evaluated.

Interfacial tension modification with hydrophilic linkers. From the previous discussion, hydrophilic linkers appear to modify the oil/water interface by adsorbing at it, but having more interaction with the aqueous phase and less interaction with the oil phase. The interfacial tension is an important parameter when characterizing interfaces and therefore would be potentially affected by linker molecules.

The interfacial tension at optimum formulation has also been related to the solubilization capacity through the Chun Huh equation (21):

$$\gamma^* = \frac{K'}{(SP^*)^2} \qquad [5]$$

where SP* is the solubilization parameter as calculated by Equation 1, γ^* is the interfacial tension at the optimum formulation, and K' is a constant.

Whereas Equation 5 can be used for pure surfactant systems, for surfactant mixtures one is faced with the challenge of correlating the mass of different surfactants. For these kinds of systems, it is more convenient to use the characteristic length (ξ) (22,23):

$$\xi = \frac{6\phi_O\phi_W}{\sum a_i n_i} V_M \qquad [6]$$

where ϕ_O is the volume fraction of oil at the middle phase, ϕ_W is the fraction of water, V_M is the volume of the middle phase, a_i is the area per molecule of surfactant i adsorbed at the oil/water interface, and n_i is the number of moles of surfactant i adsorbed at the interface.

The value of ξ can be interpreted as the thickness of the surfactant interface and is similar to the solubilization parameter. Furthermore, the relationship equivalent to Equation 5 in terms of ξ is (22,24):

$$\gamma^* = \frac{k_B T}{6\xi^2} \qquad [7]$$

Table 4 presents the characteristic lengths of the series presented in Table 2. Interfacial tension values at optimum formulations are also presented. It can be seen that the hydrophilic linker alone (0.09 M SMDNS) shows the greatest decrease in the characteristic length compared to the blank formulation. SNS shows a slight decrease and SDBNS shows no significant modification of the length.

These observations are consistent with the hypothesis that hydrophilic linkers alone (SMDNS) adsorb at the oil/water interface but they do not interact with the oil, thereby shrinking the thickness of the interface (ξ). As expected, SDBNS, which acts as a cosurfactant, does not decrease the thickness of the interface.

For the formulations containing dodecanol, the value of ξ does not include the area of the alcohol at the interface, since it has been found not to adsorb at the interface but in the palisade layer (1,6). In these formulations, the thickness

TABLE 4
Characteristic Lengths and Oil/Middle Phase Interfacial Tensions at Optimum Formulation for Alkyl Naphthalene Sulfonate Formulations[a]

Hydrophilic linker	Concentration	Dodecanol concentration	Characteristic length (ξ) (Å)	Interfacial tension (mN/m)
Blank	0	0	110 ± 10	3.5 E–3
SNS	0.09 M	0	90 ± 10	5.0 E–3
SNS	0.18 M	0.18 M	90 ± 10	6.0 E–3
SMDNS	0.09 M	0	80 ± 9	6.0 E–3
SMDNS	0.18 M	0.18 M	140 ± 51	1.1 E–3
SDBNS	0.09 M	0	100 ± 10	4.5 E–3
SDBNS	0.18 M	0.18 M	160 ± 20	1.0 E–3

[a] For abbreviations see Table 1.

TABLE 5
Solubilization and Formulation at Optimal Salinity of Homologous Carboxylates[a]

Hydrophilic linker	*S** (% NaCl, 0.09 M of hydrophilic linker)	SP* (mL/g AMA)
Blank (4% AMA)	1.4	5.7 ± 0.7
SMDNS	3.1	5.4 ± 0.7
Hexanoate	0.9	4.6 ± 0.7
Heptanoate	1.0	4.6 ± 0.7
Octanoate	2.5	4.7 ± 0.7
Abietic acid, sodium salt	1.7	11 ± 0.7
Oleate	1.7	25 ± 0.7

[a]For abbreviations see Table 1.

of the interface increases, mainly due to the "extension" of the surfactant lipophile by the lipophilic linker effect (5,6).

Table 4 also shows the interfacial tension at optimum formulation for the naphthalene sulfonate series measured at the oil/middle phase interface at 300 K. Equation 7 predicts that as the thickness of the interface (ξ) decreases, the interfacial tension increases. SNS and SMDNS used alone show a decrease in ξ, and, as expected, these formulations show an increase in interfacial tension at the optimum formulation compared to the blank. SDBNS has a slight increase in optimum interfacial tension that can be explained by the slight decrease in interfacial thickness (ξ). The SMDNS and SDBNS formulations that included dodecanol have lower interfacial tensions as predicted from their larger interfacial thickness.

From the above discussion, one additional characteristic of hydrophilic linkers is apparent: When used alone, they decrease the overall thickness of the interface (ξ) and increase the interfacial tension. However, due to the synergistic effect with lipophilic linkers, the combined linkers can maintain or increase the interfacial thickness, thereby decreasing or maintaining the interfacial tension.

Search for alternative linkers. In the previous sections, the properties of hydrophilic linkers were studied by focusing on naphthalene-based molecules. In this section, sodium carboxylates (soaps) are evaluated for their potential as hydrophilic linkers. Sodium hexanoate, heptanoate, octanoate, and abietic acid (a cholesterol-derived acid) salts are considered, along with sodium oleate. Microemulsions were obtained with TCE and AMA (4% 0.104 M); the optimum salinity and solubilization results are summarized in Table 5.

As seen in Table 5, sodium hexanoate and heptanoate have lower optimum salinities than the blank. The difference is equivalent to the molar concentration of sodium in the hexanoate and heptanoate. In other words, these two components remain as dissolved electrolytes in solution. On the other hand, sodium octanoate increases the optimum salinity almost to the level of SMDNS, which suggests that sodium octanoate acts as a hydrophilic linker. The abietic acid and sodium oleates, which are heavier carboxylates, show lower optimum salinities than the octanoate formulation, supporting the thesis that these heavier carboxylates act as cosurfactants.

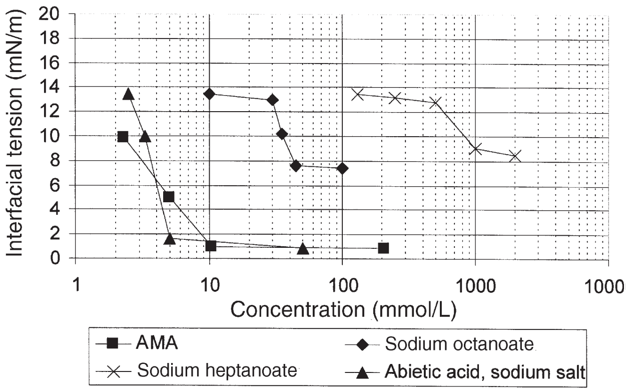


FIG. 5. Interfacial tension of carboxylates with TCE at 300 K. For abbreviations see Figure 3.

The solubilization parameter values shown in Table 5 reveal that the abietic acid and sodium oleate act as cosurfactants, similar to the role of SDBNS. Sodium octanoate has little impact on the optimum solubilization parameter. This suggests that, similar to SMDNS, sodium octanoate is adsorbed at the oil/water interface but does not enhance the solubilization due to the lack of interaction with the oil phase.

To confirm this interpretation, the amphiphile/TCE interfacial tension curves at 300 K were obtained. Figure 5 shows the results obtained, and the cmc (or apparent cmc) values are presented in Table 3 along with the areas per molecule obtained from the Gibbs equation. The sodium octanoate had a cmc four times higher than the surfactant AMA, whereas the hexanoate was two orders of magnitude higher. It seems that even with a cmc four times higher, the octanoate cmc was small enough to coadsorb at the oil/water interface with the surfactant. The abietic acid salt had a cmc lower than AMA, indicating that it not only coadsorbed at the interface, but it also interacted with the oil to lower the interfacial tension and increase solubilization of TCE. Danielsson *et al.* (14,25) have observed the synergism of octanoate and decanol, further corroborating the role of octanoate as a hydrophilic linker.

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