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Linker-Based Bio-compatible Microemulsions

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In this work we have studied the formulation of bio-compatible microemulsions using lecithin as the main surfactant and bio-compatible linker molecules (hexyl polyglucoside as the hydrophilic linker and sorbitan monoleate as the lipophilic linker). These bio-compatible systems are discussed as potential substitutes for chlorinated solvents in dry-cleaning applications and as solvent delivery systems for pharmaceutical applications. Formulation parameters and conditions were evaluated using isopropyl myristate (IPM) as the model oil. It was found that the proposed linker-based formulations were able to form alcohol-free microemulsions while achieving higher solubilization capacity than similar systems reported in the literature. In addition, these lecithin/linker formulations were able to form microemulsions with a wide range of oils, from polar chlorinated hydrocarbons to hydrophobic oils such as squalene. These microemulsions were achieved under isotonic conditions (0.9%NaCl) by only varying the relative proportions of the linkers. The "solvency" power of these bio-compatible formulations was tested for the removal of hexadecane (used as model oil) from cotton fabrics and compared to the solvency power of a typical dry cleaning solvent tetrachloroethylene (PCE). While PCE and the linker-based lecithin formulation removed the same amount of hexadecane at low loading ratios (less than 1% oil volume fraction), at higher loading ratios the linker-based lecithin formulation retained its oil removal capacity while the efficiency of the PCE system declined rapidly. These initial results thus demonstrate the remarkable oil solubilization capacity of these bio-compatible linker-based lecithin formulations and illustrate their potential as environmentally friendly replacements for organic solvents.

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Introduction

Microemulsions are widely used to enhance the solubilization of otherwise immiscible water and oil systems (*1*). In tertiary oil recovery, microemulsions are utilized to produce ultralow oil−water interfacial tensions and thus overcome the capillary forces responsible for trapping crude oil in the reservoir (*2*). Microemulsions are also widely used in surfactant enhanced remediation of oil-contaminated aquifers, in production of nanoparticles, in drug delivery systems, and in cosmetic formulations (*1*−*6*). The microemulsion must be formulated using biodegradable and bio-compatible surfactants for drug delivery systems, cosmetic formulations, personal care and cleaning products and in some surfactant enhanced remediation applications. Microemulsion systems are also being evaluated as aqueous-based "green" solvents to replace organic solvents for dry cleaning, degreasing and hard surface cleaning applications.

Because microemulsions contain domain sizes between 1 and 100 nm, they can be considered "small" vessels or nanophases for conducting reactions. In most cases these reactions involve some kind of polymerization or precipitation that occurs within the aggregate; the aggregate could be a micellar or reverse micellar microemulsion, or even a bicontinuous microemulsion. Using this technology is possible to obtain, for example nanoparticles of titania, mesoporous silica, mesoporous polymer membranes and others. A more detailed review of the different nanotechnology applications of microemulsion can be found elsewhere (*1*, *4*, *6*)

Surfactant toxicity varies with surfactant type and molecular structure. Cationic surfactants are highly toxic (*7*−*9*). Anionic surfactants can be skin irritants because of their tendency to disrupt cell membranes, and their relative toxicity depends on the molecular structure of the surfactant (*10*−*13*). Nonionic surfactants are less toxic, although nonionic surfactants of medium molecular weight and containing aromatic groups or branched hydrophobes tend to demonstrate some toxicity (*11*, *14*, *15*). In contrast, "sugar-derived" surfactants, such as the sorbitol esters, are among the most bio-compatible surfactants (*16*). Depending on the molecular structure and pH of the system, zwitterionic surfactants may be bio-compatible, showing low or no skin irritation effects and low toxicity (*17*, *18*).

Phospholipids are naturally occurring surfactant molecules that self-assemble to form cell walls. Lecithin or phosphatidyl cholines are the most relevant phospholipids as they can be easily extracted from egg yolks, soy beans and other natural sources (*19*, *20*). Lecithin is also used as a food additive capable of producing positive human health effects (*21*).

Bio-compatible Microemulsions. Formulation of bio-compatible microemulsion has been studied for over a decade, as summarized in recent review articles (*22*−*26*). Kahlweit and collaborators pioneered the use of lecithin in mixtures with medium (8−10 carbons) and long chain (12 carbons or more) alkyl glucosides in nontoxic microemulsion formulations, although they required the use of alkanols or less toxic alkenediols to obtain these microemulsions (*27*−*29*). Similar systems containing medium chain alkyl glucosides and alkanediols have been recently reported by Trotta et al. (*30*). Medium and long chain alkyl glucosides have been found to be excellent cosurfactants in microemulsions; they are also more hydrophilic and less temperature sensitive than other nonionic surfactants (*31*, *32*). For pharmaceutical applications, Malmsten (*22*) concludes that, while anionic

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microemulsion systems are typically undesirable because of the inherent toxicity of these surfactants and medium chain alcohols frequently used as cosurfactants, nonionic surfactant formulations are more bio-compatible (*22*). Malmsten states that lecithin-based formulations are especially desirable because they tend to mimic the phospholipid nature of cell walls, thus proving to be more biocompatible, except when medium chain alcohols are necessary to produce lecithin-based microemulsions (*22*, *33*, *34*). Isopropyl myristate microemulsions have also been formulated with lecithin and medium chain alcohols for drug delivery purposes (*35*−*39*).

The goal of this research is to formulate alcohol-free lecithin-based microemulsions for a wide range of oils, thus producing bio-compatible microemulsion systems that could be used in a range of applications (e.g. aqueous-based systems as alternatives to organic solvents, for use in food and drug delivery systems, and for use in cosmetic formulations). The hypothesis guiding this research is that we can produce alcohol-free microemulsion systems using lecithin as the main surfactant and bio-compatible linker molecules in the microemulsion formulation, thus achieving high oil solubilization and low interfacial tension while using bio-compatible additives.

A secondary objective of this work is to study the robustness of these systems by evaluating the effect of temperature, electrolyte and pH on the phase behavior of linker-based microemulsions. The third objective of this work is to demonstrate the ability of these linker-based bio-compatible systems to produce microemulsion systems with a wide range of oils, from polar oils such as tetrachloroethylene to more hydrophobic oils such as hexadecane and squalene. The final objective of this work is to compare the "solvency" power of linker-based lecithin microemulsions with tetrachloroethylene (PCE, a common solvent used in dry cleaning) for the removal of hexadecane used as model oil.

Linker-Based Microemulsions. Linker-based microemulsions use a lipophilic and/or a hydrophilic linker additive to modify the interfacial properties of the microemulsion system to achieve larger and/or faster solubilization (*40*−45). Graciaa and co-workers (*40*−*42*) first introduced long chain alcohols as lipophilic linkers that segregate near the surfactant tails, thereby serving to "extend" the surfactant tail into the oil and increasing the solubilization capacity of these systems. Subsequently, Uchiyama et al. (*43*) introduced the hydrophilic linker concept by introducing a surfactant-like molecule that segregates near or at the oil/water interface, but that due to its short tail offers little interaction with the oil phase (*43*). Combinations of hydrophilic and lipophilic linkers can produce a surfactant-like self-assembled system (which helps distinguish a hydrophilic linker from a cosurfactant) that offers solubilization enhancements proportional to the combined linker concentration, and that can, up to a certain point, replace the main surfactant (*43*, *45*, *46*). The linker approach has been used to formulate microemulsions for a wide range of oils in applications ranging from environmental remediation to detergent formulations (*47*, *48*).

Microemulsion Formulation. To interpret the formulation parameters we will use the surfactant affinity difference equation (SAD). This equation is a semiempirical expression that expresses the difference between the chemical potential of the surfactant in water and oil phases as a function of different formulation parameters, as follows (*2*):

$$\frac{SAD}{RT} = -\ln S + K \times \mathrm{ACN} + f(A) - \sigma + a_t(T - T_{ref}) \quad (1)$$

where S is the electrolyte concentration, K is a constant for a given surfactant (ranging from 0.1 to 0.2), and ACN is the alkane carbon number of the oil (for non-hydrocarbon it becomes EACN equivalent−ACN). The parameter $f(A)$ is a function of the alcohol/cosurfactant concentration, σ is a parameter that is a function of surfactant, a_t is a constant (~0.01 when temperature is in Celsius), and T_{ref} is a reference temperature.

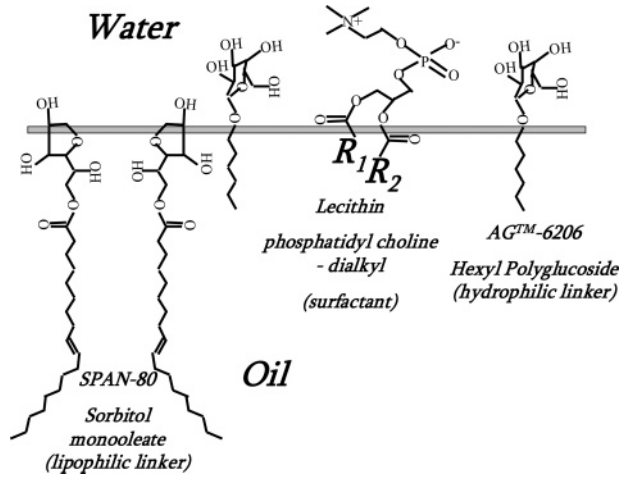

FIGURE 1. Schematic of the linker effect using bio-compatible surfactant lecithin, exemplified by phosphatidyl choline dialkyl (R1 an R2 are alkyl groups ranging from C14 to C18, see ref *36*). Hexyl polyglucoside (exemplified by hexyl glucoside) is shown as hydrophilic linker and sorbitol monoleate as lipophilic linker.

Experimental Procedures

Materials. In a previous study we evaluated the selection of a bio-compatible linkers (*49*). The linkers studied in this research were selected based on their biocompatibility: sorbitan monoleate was used as the lipophilic linker (*48*) and hexyl polyglucoside was used as the hydrophilic linker. It is important to mention that the selection of hexyl glucoside as a hydrophilic linker resulted from applying a series of characterization tests (*49*, *50*) to a range of alkyl glucoside surfactants. Hexyl glucoside was the only alkyl glucoside able to form microemulsions with lecithin while avoiding the formation of gels or stable microemulsions. This is consistent with previous study by Shchipunov et al. where they have reported the formation of gels in lecithin-dodecyl glucoside systems (*51*).

In Figure 1, lecithin, the surfactant, is represented by phosphatidyl choline dialkyl, hexyl polyglucoside is used as the hydrophilic linker and sorbitol monoleate is used as the lipophilic linker. In keeping with the linker concept, hexyl polyglucoside resides on the aqueous side of the interface (*41*, *43*) and sorbitol monoleate is shown on the oil side of the interface (*48*). Isopropyl myristate was selected as the primary oil of interest because lecithin−isopropyl myristate microemulsions have been previously studied for drug and cosmetic delivery applications (*52*, *35*−*39*).

The following chemicals were obtained from Aldrich (Milwaukee, WI) at the concentrations shown and were used without further purification: trichloroethylene (TCE, 99%+), tetrachloroethylene (PCE, 99%+), hexane (99%+), decane (99%+), hexadecane (99%+), isopropyl myristate (99%), methyl oleate (60%, technical grade), squalene (99%+), sorbitan monoleate (99%+) and sodium chloride (99%+), sodium dihexyl sulfosuccinate (SDHS, 80% aqueous solution, Fluka brand).

Laboratory grade soybean lecithin (99%) was purchased from Fisher Scientific. Soybean lecithin is a mixture of glycolipids and phospholipids produced after acetone purification; triglycerides residues account for the remaining 1%. Through selected phase behavior studies, it was confirmed that this sample of soybean lecithin has the same

TABLE 1. Selected Properties for Lecithin (Surfactant), Sorbitan Monoleate (Lipophilic Linker), and Hexyl Polyglucoside (Hydrophilic Linker)

surface active molecule	mol wt, g/mol	critical micelle concn, M	area per molecule, Å^2/molecule
lecithin[a]	~770	$\sim 10^{-10}$	~90
sorbitol monoleate[b]	428	1.8×10^{-5}	35
hexyl polyglucoside[c]	~550	1.8×10^{-2} [d]	65[d]

[a] From refs *53* and *54*. [b] From ref *56*. [c] From ref *55*. [d] From ref *49*.

TABLE 2. Selected Properties of the Oils Used in This Study

oil	EACN	mol wt, g/mol	molecular formula
tetrachloroethylene	2.9[a]	166	$Cl_2C{=}CCl_2$
hexane	6[b]	86	C_6H_{14}
decane	10[b]	142	$C_{10}H_{22}$
methyl oleate	<13[c]	296	$C_8H_{17}CH{=}CH\ C_7H_{14}COOCH_3$
isopropyl myristate	13[c]	270	$C_{13}H_{27}COOCH(CH_3)_2$
hexadecane	16[b]	226	$C_{16}H_{34}$
squalene	24[d]	423	$[(CH_3)_2CH(CH_2)_3(CH_3)CH\text{-}(CH_2)_3(CH_3)CH(CH_2)_2\text{-}]_2$

[a] From ref *43*. [b] From refs *57* and *58*. [c] From this work. [d] From ref *47*.

phase behavior as the standard Epikuron 200 soybean lecithin. The alkyl substitutes of soybean lecithin (see R1 and R2 in Figure 1) are C16:0 (13.3%), C18:0 (3%), C18:1 (10.2%), C18:2 (66.9%), and C18:3 (6.6%) where the number following the semicolon indicates the number of double bonds (*36*, *37*).

Hexyl polyglucoside AG 6206 was donated by Akzo Nobel (Chicago, IL); the product was received as a 75 wt % aqueous solution (remaining 25% water) and was used without further purification.

The molecular weight, critical micelle concentration and area per molecule of surfactant and linkers are summarized in Table 1. For lecithin, the molecular weight (*52*), critical micelle concentration (*53*), and area per molecule (*54*) can vary over wide ranges, and the reported values only correspond to average conditions. For hexyl polyglucoside, the molecular weight is an average reported by Akzo Nobel (*55*) and critical micelle and area per molecule were determined in our laboratory (*49*). The sorbitan monoleate data was taken from information readily available in the literature (*56*). Table 2 summarizes the characteristics of the oils studied in this work, including the oil EACN or equivalent alkane number (*57*, *58*).

Methods. Phase behavior studies were performed using equal volumes of aqueous solution and oil (5 mL of each). To obtain a phase transition of Winsor Type II−III−I, the concentration of hexyl polyglucoside was gradually increased (using a separate test tube for each concentration increment) while holding constant the temperature (27 °C unless stated otherwise), electrolyte concentration, lecithin and sorbitol monoleate concentration, and pressure (1 atm). This procedure will be referred to as a hexyl polyglucoside scan. Test tubes were placed in a water bath at 27 °C (unless otherwise noted), shaken once a day for 3 days, and left to equilibrate for 2 weeks. The phase volumes were determined by measuring the heights of each phase in the test tube.

Because these microemulsion systems were very sensitive to the ratio of sorbitan monoleate and lecithin, these solutions were prepared using a 20% lecithin solution in water and adding the prescribed amount of sorbitol monoleate. Another important observation is that Winsor Type I and III microemulsion systems also showed signs of algae/bacterial growth after 1 month when left at room temperature; these systems reached clear microemulsion phases within two weeks of preparation and all the characterization tests were conducted at that time. All the systems were prepared at least in duplicate with special care to follow aseptic handling procedures. Future studies will evaluate the use of small concentrations of sodium azide as a preservative.

Interfacial tensions were measured using a model 500 University of Texas spinning drop interfacial tensiometer by injecting 1−5 μL of the equilibrated middle phase in a 300 μL tube filled with the excess denser phase. The concentration of hexyl polyglucoside was determined using a UV−Vis Hewlett-Packard model 8452 diode array spectrophotometer set at a wavelength of 280 nm. Additional details of the experimental procedures can be found elsewhere (*43*, *44*, *46*, *47*, *50*).

Dynamic light scattering experiments were performed at room temperature using a BI-90 Brookhaven instrument equipped with a 35 mW red laser (wavelength ~640 nm) and a photomultiplier detector located at a 90° angle. The hydrodynamic radius and polydispersity were calculated by the equipment from the correlation function of the scattering intensity assuming that the dispersed system is an array of noninteracting spheres which allows the use of Mie scattering and the Stokes−Einstein equations to determine the hydrodynamic radius. Samples of Winsor Type I and Winsor Type II microemulsion systems were poured into standard 1-cm glass cells that were placed in the BI-90 sample holder at least 30 min before the measurement. Each sample was measured three times. The viscosity of the microemulsion phase was measured using a U-tube viscometer. The viscosity of selected samples was measured at different shear rates using a Brookfield LV-DVIII rheometer. Refraction indexes for each phase were obtained from the literature (*59*).

To test the "solvency" power of the linker-based lecithin formulations, hexadecane-stained cotton swatches (3 in. × 4 in. in size) were immersed in 50 mL of the formulation that produced a Type IV microemulsion with hexadecane (see Figure 6 at EACN = 16). The hexadecane used to stain the swatches contained 200 mg/l of red Sudan III used as a tracer to evaluate oil removal (*47*). Two set of tests were performed, one where the swatches were added sequentially (to test the ability of the formulation to retain its solvency power after several washes) and one where the swatches were added all at the same time (to simulate washing with high loads of oil). The washing solution was shaken in a Cole−Palmer table shaker (set at 300 cycles/min) at 27 °C (300 K) for 20 min. After this time the swatches were rinsed in deionized water. The oil removal efficiency was determined using a Hunterlab colorimeter measuring the intensity of the red color dissolved in the oil and applying the appropriate equations to calculate the percentage detergency (*60*). A similar procedure was used to determine the oil removal using 50 mL of tetrachloroethylene (PCE) except for the water rinsing step that was not used in this case. The detergency was determined for the organic solvent and the linker-based lecithin formulation as a function of the loading ratio expressed as the volume of oil initially present in the contaminated swatches to the volume of solvent used.

Results and Discussions

Phase Behavior of Linker-Based Isopropyl Myristate (IPM) Microemulsions. The phase behavior of linker-based IPM microemulsions was obtained by scanning the concentration of the hydrophilic component of the surfactant mixture, in this case hexyl polyglucoside. In this manner, the following transition occurred: Winsor Type II (water-swollen reverse micelles)−Winsor Type III (bicontinuous)−Winsor Type I (oil-swollen micelles) (*36*, *61*).

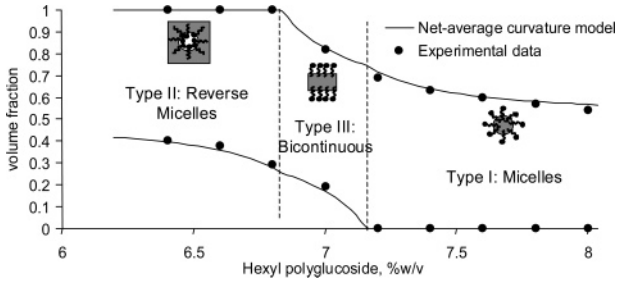

FIGURE 2. Phase behavior study of linker-based isopropyl myristate microemulsion formulated with 4% w/v lecithin, 4% w/v sorbitol monoleate, 0.9%w/v NaCl (all concentrations based in aqueous solution) at 27 °C (300 K). Oil to aqueous solution volume ratio = 1/1. Adding incremental amounts of hexyl glucoside yielded a microemulsion phase transition Winsor Type II−Type III−Type I. Solid line was obtained using the net-average curvature model (*49, 62*).

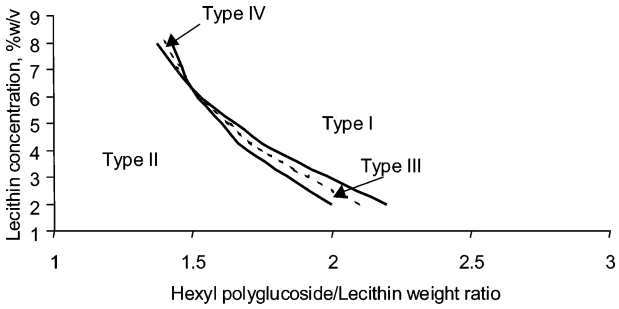

FIGURE 3. Phase map for IPM microemulsions prepared with sorbitol monoleate to lectihin weight ratio = 1/1 at 27 °C (300 K) and 0.9% w/v NaCl. Oil/water ratio = 1/1.The dotted line indicates the optimum formulation (equal volumes of oil and water solubilized in middle phase).

Figure 2 summarizes the relative phase volumes of the different water−IPM microemulsion phases that result when mixing lecithin (4% w/v or g/100 mL), sorbitol monoleate (4% w/v), electrolyte (0.9% w/v NaCl) and varying amounts of hexyl polyglucoside. The addition of incremental amounts of hexyl polyglucoside produced a phase transition of Winsor Type II−III−I as a result of the increasing hydrophilicity of the surfactant mixture.

The solid line in Figure 2 represents the phase volumes calculated using the net-average curvature model (*49*, *62*) and helps illustrate the transition that occurs with increasing hexyl polyglucoside concentrations. This net-average curvature model combines elements of critical scaling theory and statistics to predict the curvature of the surfactant membrane at the oil/water interface, using as a critical point the formulation conditions that produce a Winsor Type III microemulsion with net zero curvature. An upcoming publication will offer more details in modeling these nontoxic microemulsions and its potential use in designing cleaning, formulations and drug delivery systems. The findings in Figure 2 help confirm our hypothesis that it is possible to form alcohol-free middle phase microemulsion systems using lecithin as surfactant and a combination of bio-compatible linker molecules.

Figure 3 presents the "phase map" of IPM microemulsions where the boundaries between the different Winsor types of microemulsion phases are plotted in terms of the lecithin concentration (*y*-axis) and the hexyl polyglucoside-to-lecithin ratio (*x*-axis). From Figure 3 the Winsor Type IV single phase microemulsion required the following minimum concentrations: lecithin (6%), sorbitol monoleate (6%) and hexyl polyglucoside (*9*). When this formulation is compared with that of Corswant et al. (*36*), our combined linker formulation

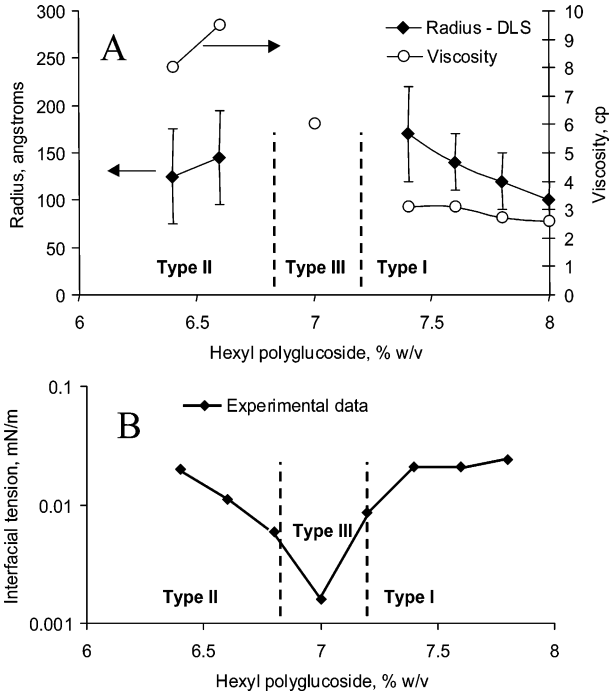

FIGURE 4. Characterization of isopropyl myristate microemulsion prepared with 4% lecithin, 4% sorbitol monoleate, 0.9% w/v NaCl, and varying amounts of hexyl glucoside at 27 °C (300 K). Oil/water ratio = 1/1. (A) Microemulsion droplet radius measured by dynamic light scattering and microemulsion viscosity. (B) Interfacial tension data.

required less lecithin and avoided the need for alcohol in the system. In addition, Moreno et al. (*63*) formulated Winsor Type I microemulsions with close to 30% lecithin+polysorbate 80 (an ethoxylated version of sorbitan monoleate) that were only capable of solubilizing 10−15% of oil (i.e., middle phase microemulsions were not achieved).

While cosurfactants interact with oil and water molecules and coadsorb with the surfactant at the interface, linker molecules interact with the surfactant and either oil or water molecules and tend to participate on only one side of the interface (*45*). Compared to cosurfactants, linker molecules have a greater partition into oil (lipophilic linkers) and water phases (hydrophilic linkers) (*50*). This phenomenon makes linkers less efficient than a typical cosurfactant (e.g., octyl glucoside used by Corswant et al.; *36*) in terms of solubilization capacity. Linker partitioning can significantly impact the appearance of the phase diagram. For example, the CMC of hexyl polyglucoside (~1%, see Table 1) suggests that at low lecithin concentration the optimum ratio of hexyl polyglucoside to lecithin must increase to account for the hexyl glucoside monomers that partition into the aqueous phase, as observed in Figure 3.

Characterization of Linker-Based IPM Microemulsions. Figure 4a presents the radius of microemulsions (Winsor Type I and II) obtained from dynamic light scattering (DLS) measurements. Microemulsion droplets increase in size as the formulation approaches the Winsor Type III bicontinuous system, which is consistent with existing microemulsion models (*49*). The droplet sizes measured using dynamic light scattering is consistent with lecithin−IPM values reported in the literature (*39*, *63*). One potential source of deviation in these measurements is that at high surfactant concentration the droplets may interact with one another changing the scattering pattern and invalidating the mathematical procedure used to calculate the size of the droplets. This potential deviation was evaluated by Moreno et al. in lecithin−IPM microemulsions (*63*), finding that at surfactant

concentrations as high as 8% droplet−droplet interactions are still negligible. The total surfactant plus linkers concentration of the system in Figure 4 is as high as 8% (based on total volume), which suggests that these deviations might also be negligible in our systems, although further confirmation of this hypothesis will be pursued in future studies.

Figure 4A also presents the viscosity of the different microemulsions. For Winsor Type I microemulsions viscosity values are two to three times the viscosity of water, while in the case of Winsor Type II systems viscosity values are close to twice the viscosity of pure IPM (~5 cP). For Winsor Type III systems, viscosity values are between the Winsor Type I and II system. Relative viscosities of 2−3 times those observed here are typical of microemulsion systems (*64*). It is worth mentioning that some of the data points where evaluated at different spinning speeds of the rheometer and the viscosity remained constant at all speeds which suggests a Newtonian-like behavior for these systems. The observed viscosity values (between 2 and 10 cP) are appropriate for most applications of interest with the exception of some transdermal applications where a higher viscosity may be desired.

One important characteristic of microemulsion systems is their ability to reduce the interfacial tension between oil and water. Figure 4B presents the interfacial tension between the different microemulsion phases and the excess phase (oil for Winsor Type I systems and water for Winsor Type II systems). The values of interfacial tension presented in Figure 4B are consistent with the large solubilization produced by these lecithin microemulsion systems, and with the low interfacial tension reported for lecithin microemulsion systems with alkanes (*34*). These low interfacial tension values are especially desirable in formulation of detergents, cleaners and aqueous solvents to replace chlorinated solvents in dry cleaning applications.

Effect of Formulation Conditions on Linker-Based IPM Microemulsions. During the application of microemulsions in drug and cosmetic delivery systems or in general cleaning applications they can be exposed to a series of changes in environmental conditions such as temperature, electrolyte concentration, and pH. For this reason we studied how the phase maps of linker-based lecithin−IPM microemulsions changed with these parameters.

According to Figure 5A, increasing the temperature from 27 to 40 °C produced a slight shift in the phase map toward lower hexyl polyglucoside-to-lecithin ratios and increases the minimum concentration of lecithin required to achieve a Winsor Type IV system (ie, decreases the system efficiency). The lower hexyl polyglucoside-to-lecithin ratio with increasing temperature indicates that the system has become more hydrophilic at higher temperatures, which is typical of an ionic surfactant system (*2*). Hexyl glucosides are relatively insensitive to temperature, which is a unique property of these surfactants (*31*, *32*).

Figure 5B presents the phase maps for IPM microemulsion with two levels of electrolyte concentration. With increasing electrolyte concentration the phase map shifts-to-lower ratios of hexyl polyglucoside to lecithin; i.e, the system transitions from Winsor Type II−III−I as with increasing temperature above. The explanation for this unusal trend is unclear and should be evaluated in future research.

The effect of pH on linker-based lecithin IPM microemulsions is demonstrated in Figure 5C. Increasing pH produces the same effect as increasing temperature or electrolyte, for example, it promotes the transition from Winsor Type II to III to I phases (i.e., the system becomes more hydrophilic). While the effect is especially significant between pH 6.5 and pH 10.7, it is more subtle between pH 3.5 and pH 6.5. This can be explained by the fact that the lecithin has a positive charge below pH 3 (the isoelectric point of lecithin) and is anionic at pH values larger than 5.2

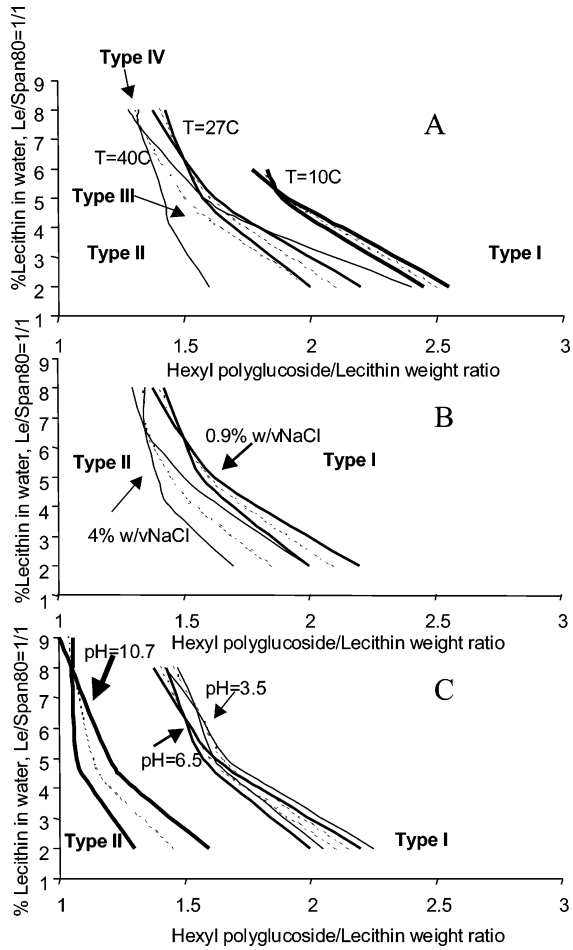

FIGURE 5. Phase maps for linker-based lecithin microemulsions for IPM at different formulation conditions. (A) Temperatures (10, 27, and 40 °C). (B) Electrolyte concentrations 0.9% and 4.0% w/v. (C) pH values of 3.5, 6.5, and 10.7. IPM microemulsions prepared with sorbitol monoleate to lectihin weight ratio = 1/1. Baseline conditions 27 °C (300 K), at 0.9% w/v NaCl and neutral pH (pH ~6.5). Oil/water ratio = 1/1.

(pK_b for lecithin) (*65*, *66*). Thus, at pH 3.5 lecithin has both negative and positive charges that can make it highly hydrophobic. At pH 6.5 the system is slightly more anionic but not enough to make a dramatic change in the phase behavior. However, at pH 10.7 lecithin becomes fully anionic which is reflected in a significant change in the phase map in Figure 5C.

Linker-Based Lecithin Microemulsion with a Variety of Oils. Linker-based lectihin microemulsion were also developed for a wide range of oils (see Table 2). Figure 6 presents the minimum lecithin concentration and the hexyl polyglucoside-to-lecithin ratio required to achieve a Winsor Type IV microemulsion, as a function of the oil's equivalent alkane carbon number. As the oil becomes more hydrophobic (higher EACN), the minimum lecithin concentration increases, as is typical for microemulsion systems (*2*), and the hexyl polyglucoside-to-lecithin ratio (AG-6/le) decreases in a linear manner, which when incorporated into eq 1 (*2*) results in eq 2 (where b is a constant and other variables are defined above):

$$\frac{SAD}{RT} = -\ln S + K \times \mathrm{EACN} + f(A) - \sigma + a_t(T - T_{ref}) + b(\mathrm{AG\text{-}6/le}) \quad (2)$$

This expression is extremely useful to model the phase behavior of microemulsions (*49*).

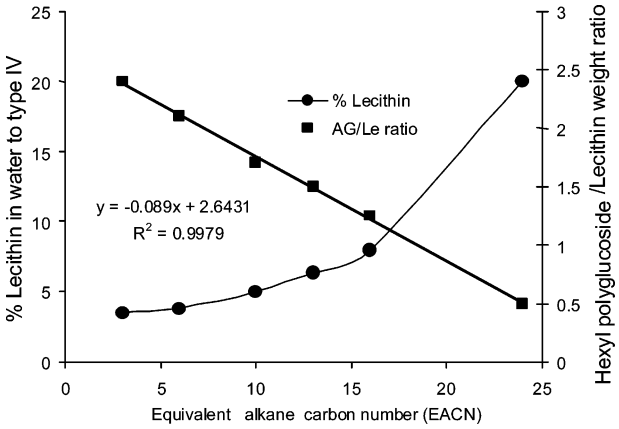

FIGURE 6. Formulation of linker lecithin microemulsion with a wide variety of oils, indicating the hexyl polyglucoside-to-lectihin ratio to achieve a single phase microemulsion and the minimum amount of lecithin required to form a single phase microemulsion. Other conditions: sorbitol monoleate-to-lecithin ratio 1/1, temperature 27 °C (300 K), 0.9% w/v NaCl. Oil/water ratio = 1/1. EACN values for each oil presented in Table 2.

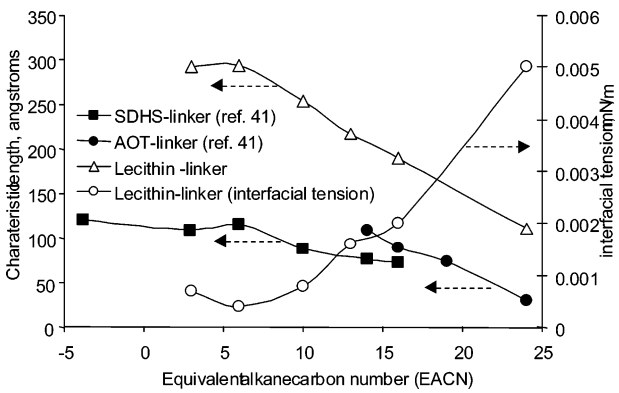

FIGURE 7. Properties of linker lecithin microemulsion with a wide variety of oils, indicating the characteristic length and interfacial tension of the microemulsions whose formulation is described in Figure 6. The characteristic length for AOT and SDHS linker microemulsions obtained from Acosta et al. (*47*).

Figure 7 presents the characteristic length and the minimum interfacial tension for the optimum formulations reported above. The characteristic length defines the zone of impact (thickness) of the surfactant at the oil/water interface in the bicontinuous middle phase microemulsion (*62*, *67*):

$$\xi = \frac{6\phi_o\phi_w V_m}{A_S} \tag{3}$$

where ϕ_o and ϕ_w are the volume fractions of oil and water in middle phase microemulsion, V_m is the volume of the middle phase, and A_S is the interfacial area, provided by the surfactant adsorption that can be calculated as (*63*):

$$A_S = \sum_i V_{w,o} Cs_i \times \phi_i \times 6.023 \times 10^{23} \times a_i \tag{4}$$

where $V_{w,o}$ is the initial volume of the aqueous solution containing the surfactant and linkers, Cs_i is the initial aqueous molar concentration of the surfactant, cosurfactant, and hydrophilic linker added to the formulation, ϕ_i is the fraction of the surfactant/cosurfactant that is present in the middle phase microemulsion, and a_i is the area per molecule of the species considered (in Å^2/molecule). Because the systems presented in Figures 6 and 7 correspond to Winsor Type IV

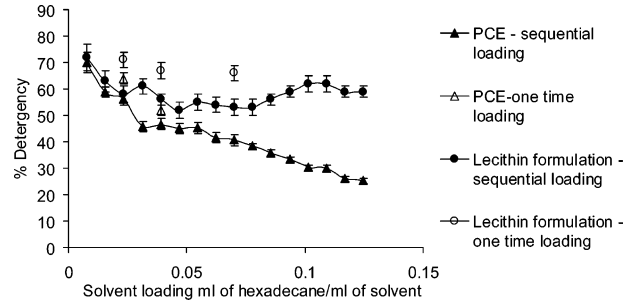

FIGURE 8. Detergency of hexadecane from cotton swatches using a linker-based lectihin formulation (8% lecithin, 8% sorbitol monoleate, and 10% hexyl polyglucoside and 0.9% NaCl at 27 °C (300 K)) and PCE as a function of hexadecane to solvent loading ratio for sequential and one-time loading tests.

single phase microemulsions all values of ϕ_i are equal to 1 (no excess phases to partition into). Also, in contrast to common lipophilic linkers, sorbitol monoleate is more surface active than its alcohol counterparts, and thus the area per molecule of this group (see Table 1) is also considered in A_S. The characteristic length decreases as the oil becomes more hydrophobic (Figure 7), which indicates that less oil is associated with or solubilized by the microemulsion; this trend is commonly observed for microemulsions (*47*).

For comparison, Figure 7 also shows the characteristic length of microemulsions formulated with sodium dihexyl sulfosuccinate (SDHS) and sodium bis(2-hexyl)dihexylsulfosuccinate (AOT) as surfactants, SMDNS as a hydrophilic linker and oleyl alcohol as lipophilic linker. For most cases the characteristic length of linker-based lecithin microemulsions is more than twice the characteristic length of the alkyl sulfosuccinate microemulsions. The greater solubilization in lecithin microemulsions is attributed to the longer extended tail of lecithin (between 14 and 18 carbons) when compared to that of SDHS and AOT (six carbons). In addition, for lectihin-based microemulsions it was possible to maintain optimum conditions even while the electrolyte concentration was kept constant at a value of 0.9% NaCl (isotonic solution), while for the alkyl sulfosuccinated surfactants the electrolyte level went to unacceptable values of 16% NaCl for the most hydrophobic oils.

The interfacial tension values presented in Figure 7 are well below values reported for microemulsion systems produced with alkyl sulfosuccinated surfactants (*47*); this is consistent with the higher solubilization values of lecithin-based microemulsions. These interfacial tension values are similar to those produced by others with medium chain alcohols as cosurfactants and alkanes as the oil phase (*34*); thus, our alcohol-free systems performed very well.

Linker-based lecithin middle phase microemulsions of methyl oleate were only achieved at temperatures of 60 °C or larger; at lower temperatures atypical two-phase systems were obtained. At 60 °C the methyl oleate system achieved a Winsor Type IV single-phase microemulsion with only 6% lecithin at an hexyl polyglucoside-to-lecithin ratio of 1.4. For the same conditions IPM formed a single-phase microemulsion at lower hexyl polyglucoside-to-lecithin ratios, which, according to the trends in Figure 6, indicates that methyl oleate has a lower EACN than IPM. Graciaa et al. reported that ethyl oleate (a similar molecule to methyl oleate) showed polar behavior, segregated near the surfactant tail like a lipophilic linker, and had an EACN value of 6 (*68*). Further research is necessary to explore the role of ester groups on the formulation of linker-based lecithin microemulsions.

Lecithin-Based Microemulsion Systems as Alternative to Dry Cleaning Solvents. Figure 8 compares the detergency of hexadecane from 100% cotton swatches using a lecithin formulation as an aqueous solvent (containing 8% lecithin,

8% sorbitol monoleate and 10% hexyl polyglucoside with 0.9% NaCl) and using tetrachloroethylene (PCE) as an organic solvent typically used in dry cleaning applications. The detergency performance is plotted as a function of the solvent loading ratio, which is calculated as the total volume of hexadecane in the swatches divided by the solvent volume (50 mL). The swatches were washed under two different conditions: one where the swatches were sequentially washed (using the same solvent to simulate solvent reuse without purification), and another where the swatches were added to the container all at the same time (to simulate one time use with high loading conditions). In both cases the lecithin formulation and PCE have comparable detergency at low loading conditions (at or less than 0.02 volume ratios), but lecithin outperforms PCE at high loading conditions.

Hexadecane is completely miscible in PCE, and lecithin can form a Winsor Type IV system with hexadecane. The maximum loading of hexadecane for the lecithin single phase microemulsion will be a volume fraction of 1; thus it is not surprising that at ratios of 0.13, the lecithin formulation stills maintain its high removal efficiency. On the other hand, it was surprising that the organic solvent decreased in cleaning efficiency at relatively low loading ratios. This can be explained on the basis that when the cotton swatch is extracted from the container it still contains significant amounts of the PCE solution trapped between the fibers and once the PCE evaporates, the less volatile hexadecane is left trapped between the fibers. In the case of the lecithin formulation, the oil removed is either solubilized in micelles or liberated from the fibers by typical detergency mechanisms such as roll-up and snap-off (*60*). Since the water is the continuum phase, once the oil is liberated it has a little chance to re-deposit on the surface of the fabric because it becomes trapped in the hydrophobic core of the micelles. Similar to PCE solution, a certain amount of surfactant solution remains trapped between the fibers, but after the rinsing step, the residual hexadecane trapped in micelles is liberated.

These preliminary results support the idea that concentrated surfactant solutions with high oil solubilization capacity can be used as aqueous-based solvents without decrease in oil removal. There are other important factors not addressed here, such as shrinkage and wrinkling that are important for hydrophilic fibers such as wool. Future research will look at these effects and evaluate the use of alternative surfactant formulations and the economic aspects of using microemulsion systems as aqueous-based alternatives to organic solvents.

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