# Physicochemical Behavior of Mixed Surfactant Systems: Petroleum Sulfonate and Lignosulfonate

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**ABSTRACT:** The physicochemical properties of mixed polymeric surfactant systems were studied with different techniques. A binary system consisting of lignosulfonate and petroleum sulfonate and a ternary system consisting of two different lignosulfonates and petroleum sulfonate were studied with respect to phase behavior, interfacial tension, specific conductivity, and pH measurements. In addition, the original lignosulfonates were subjected to ion exchange from sodium to calcium or vice versa, and the effects were investigated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 860–865, 2003

**Key words:** interfacial tension; petroleum sulfonate; lignosulfonate; mixed surfactants; aging

## INTRODUCTION

In continuation of our renewed interest in the combined petroleum sulfonate (PS) and lignosulfonate (LS) systems used in enhanced oil recovery, we studied here various physicochemical properties of mixed PS and LS systems. PS, a petroleum-based surfactant, has been widely employed as a surfactant for enhanced oil recovery. LSs, which are wood-based, water-soluble, polydispersed polyelectrolytes, are anionic, surface-active derivatives of lignin. Although LS are very strong electrolytes, they differ from conventional electrolytes in their high molecular weights and in their polydispersity as polymers.

Recently, purified and modified LSs have attracted both academic and industrial interest as inexpensive new materials with improved properties. Their applications are found in the fields of enhanced oil recovery, food additives, adhesives, and others. Large quantities of LSs have been used as inexpensive preflush chemicals to reduce the loss of more expensive surfactants on active adsorption sites in the field application of surfactant flooding in oil reservoirs.[1–4] In another application, modified LS thinner, Fe–tannin–LS, prepared by crosslinking LS with naturally occurring tannin extract in the presence of formaldehyde and chelating with ferrous ions, has been found to have better thinning ability and resistance to elevated temperatures compared to the commonly used FeCr–LS thinner.[1] In another application, a high sur-

face activity of oxidized LS, which could be substantially increased by an increase in the content of carbonyl groups, reduced the surface tension of binder solutions and facilitated the distribution of wood particles. Such modified LSs find use as wood adhesives.[4]

Past research in this laboratory has focused on LS as an additive to PS in enhanced oil recovery.[5–14] Hornof studied the effect of adding LS to PS on interfacial tension (IFT) against various hydrocarbons. Their results showed that the largest reduction of IFT was observed with *n*-heptane, regardless of the surfactant formulations.[5] With the help of spinning drop tensiometer measurements, Son et al. found that ultralow IFTs against oil (<0.01 mN/m) could be attained with mixed PS/LS solutions.[7] Chiwetelu et al. proposed a synergistic mechanism for the high activity of PS/LS surfactant mixtures.[8] They found that PS/LS mixed surfactants were very effective in moving residual oil from model oil reservoirs. The addition of LS to PS resulted in the further reduction in IFT of between 60–90%, but this effect was accompanied by a marked increase in viscosity. Manasrah et al. proposed that molecular aggregates involving liquid crystalline structures are formed in the mixed PS/LS solutions on the basis of viscosity, electrical conductivity, and phase behavior.[9,10] PS interacts with dissolved salts and various cosurfactants to form more or less organized structures, including liquid crystalline structures. Kumar et al. found that mixed surfactant systems containing divalent cations gave faster coalescence behavior compared to those involving a univalent cation.[11] In another study, water-soluble polymer additives significantly influenced the dynamic IFT behavior of a reacting oil–water system as monitored by spinning drop tensiometer measurements.[14] IFT decreased as the concentration of water-

soluble polymer [poly(vinyl alcohol) or polyacryl-amide] additive increased in the case of linoleic acid in a paraffin oil mixture against distilled water, whereas the IFT increased as the concentration of water-soluble polymer additive increased in the case of linoleic acid in a paraffin oil mixture against aqueous NaOH solution.

Recent work conducted by Chiu and Kuo[3] showed that there is a correlation between low IFT and the micellar size of PS. PS forms a microemulsion with crude oil with a droplet size of approximately 100 nm. Our previous experiments have shown that the addition of LS to PS affects its phase behavior and related properties. Consequently, PS/LS mixed surfactant systems have received renewed interest in this laboratory. The purpose of this work was to investigate the behavior of mixed PS/LS solutions. The properties studied included: IFT against iso-octane as a model oil, phase behavior, specific conductivity (SC), and pH. In addition, sodium-based LSs were ion-exchanged to calcium-based LSs, calcium-based LSs were ion-exchanged to sodium-based LSs, and the effects of the change of counterion were investigated.

## EXPERIMENTAL

### Materials

The commercial LSs used in this study were Marasperse N-22 (mainly sodium salt: 6.7% Na$^+$ and 0.6% Ca$^{2+}$ as reported by the manufacturer) and Marasperse C-21 (mainly calcium salt: 4.0% Ca$^{2+}$ and 2.1% Na$^+$ as reported by the manufacturer). Both were commercial products manufactured by the former American Can Co. (Greenwich, CT). Samples Marasperse C-21* (sodium salt) and Marasperse N-22* were prepared by ion exchange from Marasperse C-21 and Marasperse N-22, respectively. The commercial PS used here, Petrostep-420, was supplied by the Stepan Chemical Co. (Northfield, IL). It was a tarry and semi-solid material, which was completely soluble in water. It contained 4.1% inorganic salt with Na$^+$ as the counterion. Iso-octane, supplied by Eastman Organic Chemicals (Rochester, NY), was used as the model oil for IFT measurements.

### Procedures

Details pertaining to the preparation of solutions and system equilibration were given by Son et al.[7]

A University of Texas (Austin, TX) spinning drop tensiometer (model 300) was used for the determination of IFT. All measurements were carried out at room temperature (23 ± 1°C). IFT measurements were conducted with iso-octane as the model oil phase. An Anton Parr (Graz, Austria) digital densitometer was

**TABLE I**
**Formulation of the Systems Investigated in This Study**

| System | Composition |
|--------|-------------|
| System A | Sodium-based LS (N-22) and PS |
| System B | Sodium-based LS (C-21*) and PS |
| System C | Calcium-based LS (C-21) and PS |
| System D | Calcium-based LS (N-22*) and PS |
| System E | Sodium-based LS (N-22), sodium-based LS (C-21*), and PS |
| System F | Sodium-based LS (N-22), calcium-based LS (C-21), and PS |

used to measure the corresponding liquid density that was needed to calculate IFT.

SC measurements were carried out with a Reddick Zeta meter electrophoresis cell supplied by Zeta Meter Inc. (New York, NY) SC was calculated from the following equation:

$$SC = kI/V \ (\mu\Omega/cm)$$

where $k$ is the cell constant, $I$ is the current ($\mu$A), and $V$ is voltage (V).

## RESULTS AND DISCUSSION

Two different mixed surfactant formulations were used in this work, one containing PS and LS, and the other containing PS in a mixture with two different LSs. On the basis of earlier studies, the concentration of PS was fixed at 0.2 wt %, and the concentration of NaCl (i.e., the salinity of the aqueous solution) was also maintained constant at 1.5 wt %. The NaCl concentration (i.e., 1.5 wt %) was below the optimum concentration (~2.5–3 wt %) to lower IFT. However, at 1.5 wt % NaCl concentration, the largest viscosity increases have been recorded.[11] It is evident that there is a certain LS concentration at which maximum viscosity will occur for a fixed PS concentration. Three different LS concentrations were subsequently used and are specified in the discussion describing the specific systems. The fluid systems used in this study are listed in Table I.

### Binary mixtures

In this study, the concentration of LS was varied from 0 to 0.2 wt %, whereas the concentration of PS was fixed at 0.2 wt %. The salt concentration (NaCl) was also constant at 1.5 wt %. The IFT, SC, and pH behaviors of two binary mixtures containing sodium-based LSs (N-22 and C-21*) with PS (systems A and B) and calcium-based LSs (C-21 and N-22*) with PS (systems C and D) are shown in Figure 1. Calcium-based LSs appeared to be more interfacially active than sodium-based LSs. Thus, the presence of the divalent calcium
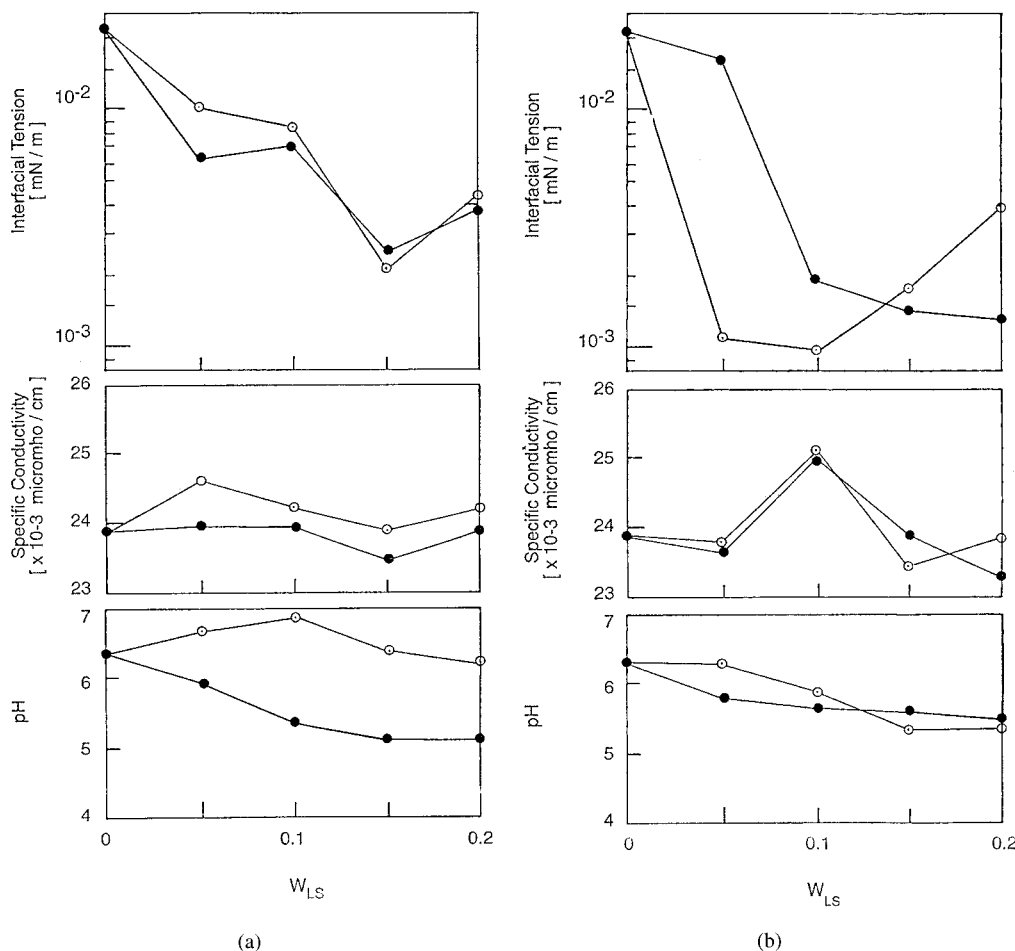
**Figure 1**  Dependence of IFT, SC, and pH on the weight fraction of (a) sodium-based LS [(○) system A and (●) system B] and (b) calcium-based LS [(○) system C and (●) system D].

ions in the calcium-based LSs appeared to enhance the interfacial activity of these mixed surfactant systems in comparison to those in the univalent sodium-based LSs, as reported previously.[11] Again, a higher IFT was observed for a higher total concentration of ions for all cases. The IFT value for LS composition [weight fraction of lignosulfonate ($W_{LS}$) = 0–0.1] was higher for system A (containing N-22) compared to system B (containing C-21*), although both were sodium-based LSs. Similarly, for the calcium-based LSs, the IFT value for LS composition ($W_{LS}$ = 0–0.1) was higher for system D (containing N-22*) than for system C (containing C-21).

The effects of $Ca^{2+}$ and other divalent ions on the phase stability of PS are very important in enhanced oil recovery. Some studies have shown PS to be ineffective in the presence of $Ca^{2+}$ because of the precipitation of the surfactant.[15] The difference between $Na^+$ and $Ca^{2+}$ is due to a different effectiveness in reducing the repulsions caused by electric double layers. The double layer is suppressed to a larger extent by the divalent ion, resulting in agglomeration and precipitation.

To facilitate understanding of structural changes, SC measurements were carried out. SC is known to drop when more tightly packed lamellar crystalline structures begin to form.[10] It seemed that in this system, there was a loosely packed structure of micelles composed of ionized molecules that had liquid crystalline structure.

The SC change observed with composition for both types of the sodium-based LS and PS mixtures (systems A and B) was small. The SC of the system A (N-22 + PS) was slightly higher than system B (C-21* + PS) because of a greater $Na^+$ concentration in the former. There was an increase in SC for both calcium-based LS and PS mixtures [system C (C-21 + PS) and system D (N-22* + PS)]. This was associated with the formation of two-phase structures, and at higher LS concentrations, a decrease in the SC value could be explained by liquid crystalline structure formation. The liquid crystalline PS–LS–$Ca^{2+}$ aggregates were responsible for the low SC, as reported earlier.[15]

Further support in evidence of the structural changes in the solution was obtained through pH
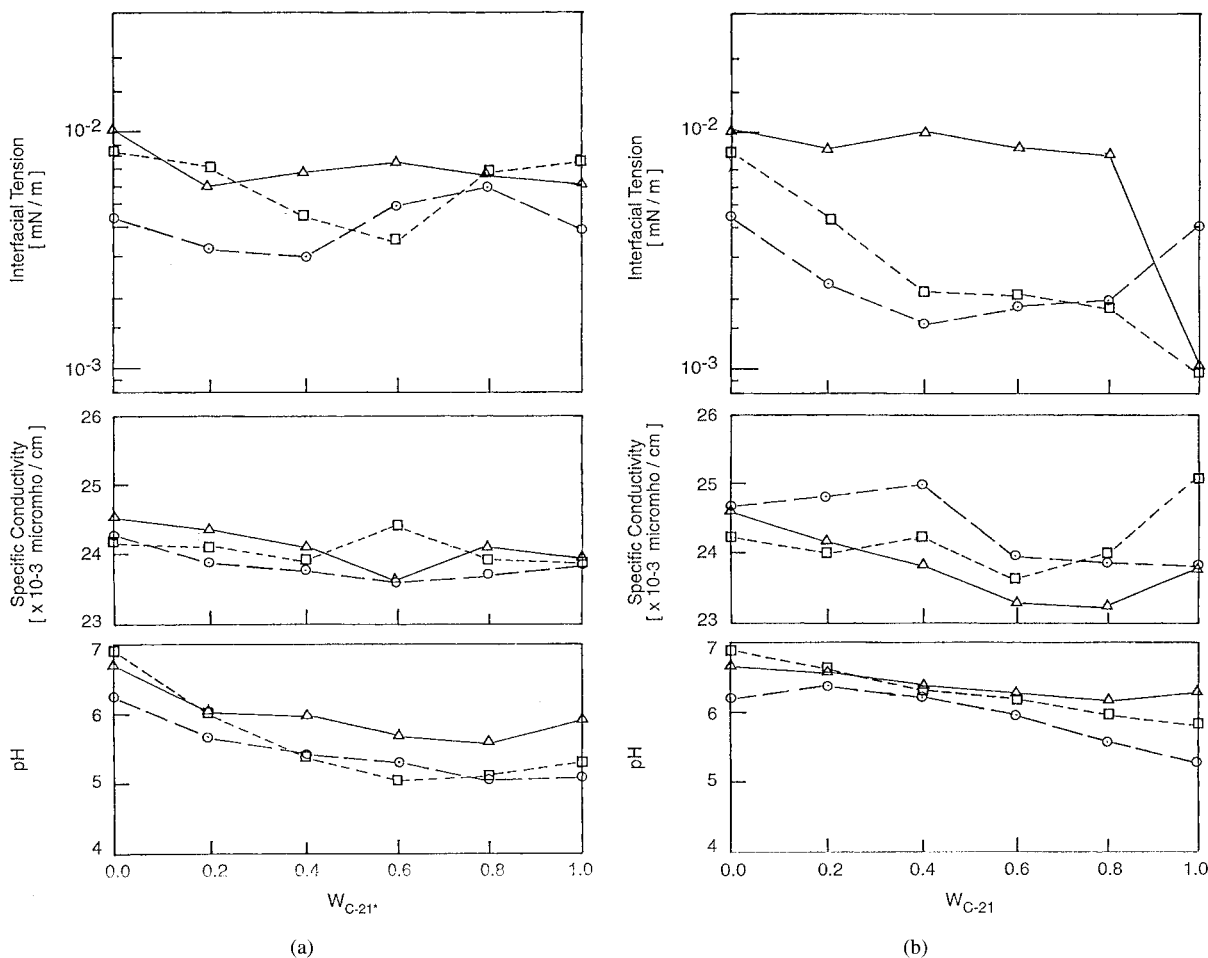
**Figure 2** Dependence of IFT, SC, and pH on the weight fraction of (a) sodium-based LS C-21* in system E and (b) calcium-based LS C-21 in system F for three different concentrations: ($\triangle$) 0.05, ($\square$) 0.1, and ($\bigcirc$) 0.2 wt % total LS mixture.

measurements. The behavior seemed to suggest that there existed a counterion exchange reaction between $Na^+$ in PS with $Ca^{2+}$ in calcium-based LSs and between $Na^+$ in sodium-based LSs with $Ca^{2+}$ in calcium-based LSs. Once again, there was a possibility of cation association with micelles due to the presence of electrostatic forces.[16] When a more tightly packed lamellar liquid crystalline structure is being formed, the pH drops. The differences between the individual systems were small, however, and no definitive conclusions could be drawn.

**Ternary mixtures**

IFT, SC, and pH behaviors of two ternary mixtures were studied. These contained different proportions of two sodium-based LSs (N-22, and C-21*) and PS (system E) and a sodium-based LS (N-22), a calcium-based LS (C-21), and PS, (system F). The results are depicted in Figures 2. In each system, three different total LS concentrations (0.05, 0.1, and 0.2 wt %) were used. Because most natural connate (or interstitial) waters in petroleum reservoirs contain both $Na^+$ and $Ca^{2+}$ to-

gether, the study of the mixtures of both ions is of practical interest.

For system E (N-22 + C-21* + PS), the IFT value did not vary much with LS composition. At the lowest total LS concentration (0.05 wt %), the IFT value initially decreased, and afterward, the IFT value became almost constant with changing LS composition. At the middle total LS concentration (0.1 wt %), the IFT value decreased until the LS composition reached a weight fraction of C-21* in the LS mixture ($W_{C-21*}$) of 0.6 and then increased. At the highest total LS concentration (0.2 wt %), the IFT value initially decreased up to a $W_{C-21*}$ of 0.4, then increased up to a $W_{C-21*}$ of 0.8, and then again decreased for pure LS (C-21*). However, for system F (N-22 + C-21 + PS), the IFT study showed that it seemed to be slightly more interfacially active than system E (N-22 + C-21* + PS). Thus, the presence of the divalent calcium ions in the calcium-based LS appeared to enhance the interfacial activity of these mixed surfactant systems compared that of univalent sodium-based LSs, as reported previously.[15] At the lowest total LS concentration (0.05 wt %), the IFT value was the highest among other compositions
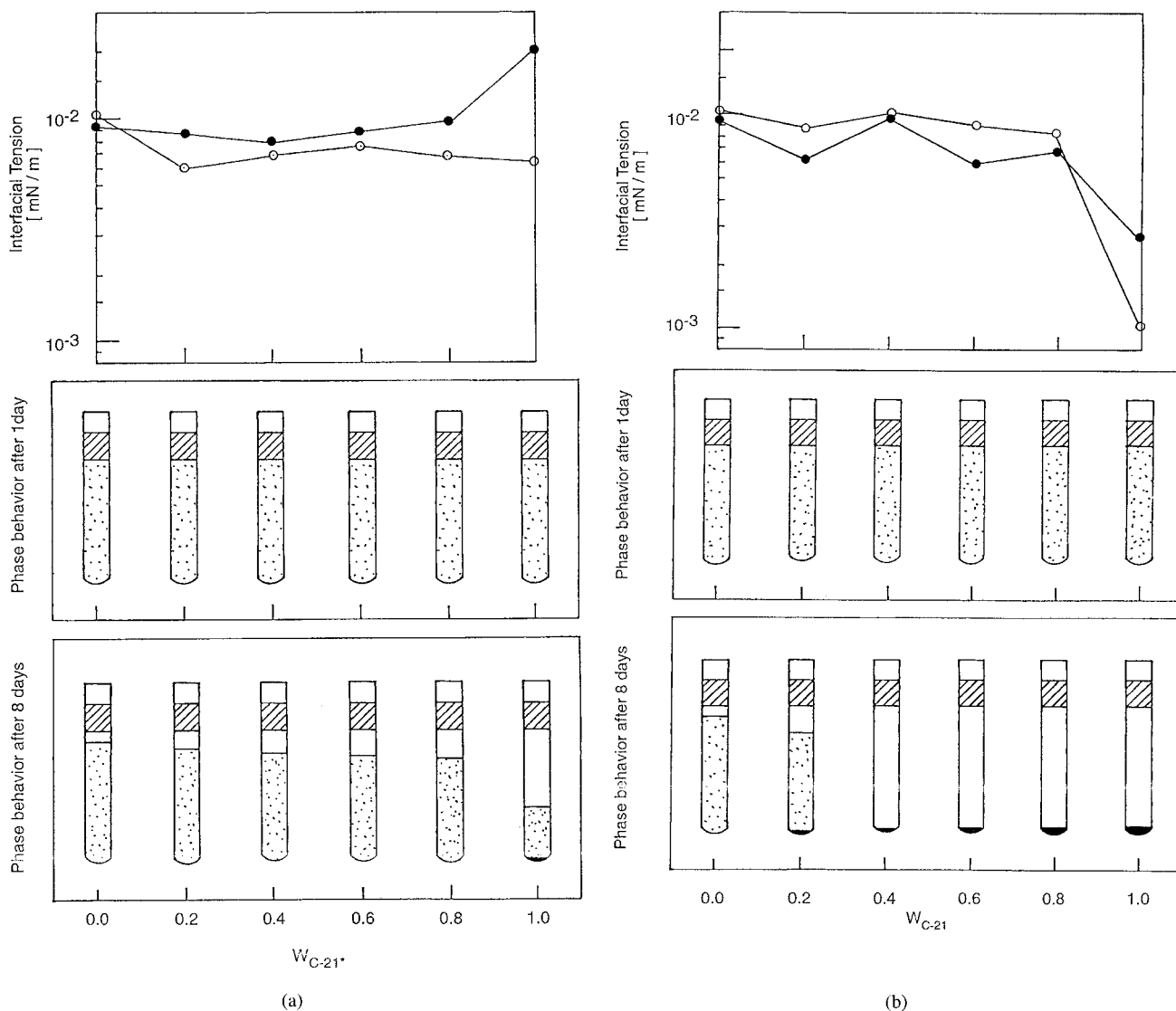
**Figure 3** Dependence of IFT and phase behavior on the weight fraction of (a) sodium-based LS C-21* in system E and (b) calcium-based LS C-21 in system F for a 0.05 wt % total LS concentration: (○) 1 and (●) 8 days.

and almost constant with changing LS composition except for pure LS (C-21). At the second total LS concentration (0.1 wt %), the IFT value decreased until the LS composition had a weight fraction of C-21 in the LS mixture ($W_{C-21}$) of 0.4. Then, the IFT value was almost constant up to a $W_{C-21}$ of 0.8, the lowest IFT value was observed for pure LS (C-21). At the highest total LS concentration (0.2 wt %), the IFT value decreased up to a $W_{C-21}$ of 0.4 and then increased with changing LS composition.

SC observed for system E (sodium-based LSs) was similar to that of systems A and B. With increasing total LS concentration in the mixture, the SC value appeared to decrease slightly, but the measured values of SC were very close. However, there existed a strong correlation between the concentrations of LS and SC in system F. At the lowest total LS concentration (0.05 wt %), the SC value initially decreased with

increasing $Ca^{2+}$ concentration (calcium-based LS C-21), but later, it increased. At the middle total LS concentration (0.1 wt %), the SC values also initially decreased with $Ca^{2+}$ concentration and, subsequently, increased abruptly. This phenomenon could be explained by the formation of liquid crystalline PS–LS–$Ca^{2+}$ aggregates, as mentioned previously. After a certain $Ca^{2+}$ concentration was reached, a liquid crystalline structure was formed. At the highest total LS concentration (0.2 wt %), the SC values initially increased with $Ca^{2+}$ concentration and, subsequently, the SC values decreased. We concluded that a clear correlation between LS concentration and SC could be detected in system F but not in system E.

The pH values observed in systems E and F decreased somewhat with increasing proportion of the C-21 product, both in its original sodium form and in the calcium form obtained by ion exchange. With in-

creasing total LS concentration in both systems, the pH values decreased. Once again, the effects were relatively small.

### Aging study

Aging studies were conducted by measurement of the IFT of the PS–LS surfactant systems against iso-octane as a model oil and by the visual observation of the phase behavior after 1 and 8 days equilibration. The upper (lighter) layer was iso-octane (the oil phase), and the bottom layer was the aqueous phase with the LS and PS mixture. As mentioned by Son et al.[7] a special procedure was used in the case of the formation of a third phase: any precipitate or opaque layer formed in the aqueous phase was thoroughly mixed with the rest of the aqueous phase before IFT measurements were conducted.

The results obtained for systems E and F are shown in Figures 3. The total concentration of LS was 0.05 wt %. For system E, the IFT value was almost invariant with LS composition, and it was also little affected by the phase behavior. A single homogeneous aqueous phase was observed after 1 day, but as the system aged, the phase behavior became more complex. After 8 days, the aqueous phase separated into a clear upper phase and a translucent (colloidal) layer, which eventually gave rise to a solid precipitate in some cases. This behavior was more pronounced in system F, which contained calcium-based LSs. However, the phase behavior had little effect on the observed IFT. For system E, the IFT value after 8 days was only slightly higher than that observed after 1 day of equilibration. For system F, the IFT measured after 8 days was slightly lower than that for 1 day. The IFT value of the system containing pure LS (C-21), however, was much lower compared to those of the other LS compositions. The reason for this behavior was not clear,

but it may have been caused by inadequate homogenization of the aqueous solution.

### CONCLUSIONS

A synergistic IFT behavior was observed for both sodium-based and calcium-based LSs in LS–PS mixtures. The bivalent $Ca^{2+}$ ion had an important role in the determination of the IFT value compared to the univalent $Na^+$ ion. With a certain concentration of $Ca^{2+}$ ions, a liquid crystalline structure appeared to form, as evidenced by IFT and SC measurements for both binary and ternary systems. An aging study indicated that the IFT was almost constant up to 8 days for all LS compositions, but the phase behaviors were more complex, and several phases were formed.

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