Synthesis and Characterization of Surfactants *via* Epoxidation of Tall Oil Fatty Acid

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ABSTRACT: The synthesis and characterization of novel surfactants derived from tall oil fatty acid methyl esters are presented. The tall oil fatty acid methyl esters, which mainly contain methyl oleate, were converted to 9,10-epoxy derivatives and further transformed to the 9 (or 10) polyethylene glycol (PEG) ethers. Compounds with three different monomethylated PEG chain lengths with molecular weights of 350, 550, and 750, corresponding roughly to 7, 11, and 16 ethylene oxide units, were prepared. Surfactants were formed at an 89% overall yield from tall oil fatty acid. Cloud points were 46, 63, and 84°C, respectively, and surface tensions at the CMC (2.0, 1.0, and 0.4 mM, respectively) varied from 33 to 38 mN/m. Equilibrium surface tension and reflectometry measurements were made and results were similar to those of conventional long alkyl chain PEG surfactants. Results of the tensiometry and reflectometry measurements showed that the surfactants aligned better at the air–water interface than conventional surfactants. The adsorption properties for the three surfactants were similar to those of polyoxyethylene glycol alkyl ethers.

Paper no. S1286 in *JSD* 6, 47–53 (January 2003).

KEY WORDS: Epoxide, PEG, reflectometry, surface tension, surfactants, tall oil fatty acid.

In recent years there has been a great interest in surfactants derived from natural products, including sugars (1,2), sterols (3), and fatty acids (4). The use of naturally occurring raw materials is believed to provide improved biodegradability. Furthermore, renewable sources are necessary for long-term sustainable production. As a part of a research program entitled Surfactants Based on Natural Products, the possibility of using fatty acids as a starting material for new types of surfactants was investigated. This report describes the synthesis of three new surfactants based on tall oil fatty acids. Previously known reaction steps have been modified and combined in a new way to find an industrially applicable synthetic route. Neat reactions, reasonably

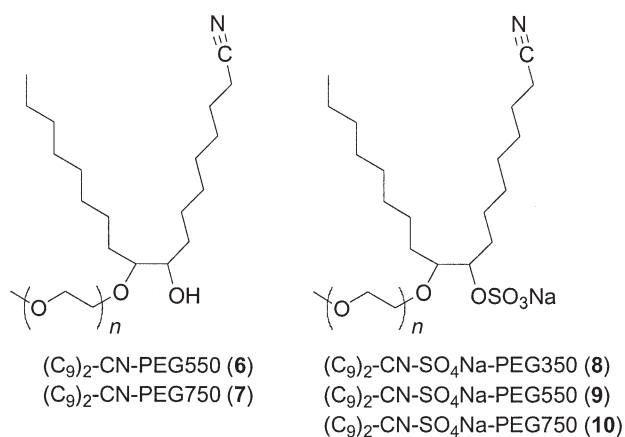high yields, and the absence of poisonous chemicals were considered important.

The initial idea of the present work was to investigate the possibility of using the unsaturated double bond on a fatty acid as a starting point for the reactions instead of the often-used carboxylic group. A reaction of this type would result in a nonionic surfactant with two branches of hydrophobic chains. The choice of tall oil fatty acid as a starting material was mainly due to its ready availability as a natural product with a relatively low price and a high degree of unsaturation (<5% saturated acids).

To obtain a nonionic surfactant, the carboxylic group must be protected. The simplest way is to make a methyl ester. Direct esterification requires a large excess of methanol, and its low boiling point demands a long reaction time or a pressurized reactor (5). Hence, a novel esterification procedure suitable for industrial production was developed. Fatty acid methyl esters are usually epoxidized either from peracetic acid (6,7) or from hydrogen peroxide and a suitable catalyst (Scheme 1). In this synthesis an Ishii–Venturello epoxidation (8,9) was used to avoid the tedious removal of acetic acid formed in peracetic epoxidation. An improvement on the original Venturello epoxidation was used, where the catalyst was formed *in situ* (10).

Previously, twin-chained surfactants of very similar molecular structures were prepared and studied using a nitrile group instead of the ester group (11). Additionally, gemini

SCHEME 1

$(C_9)_2$-CN-PEG550 (**6**)
$(C_9)_2$-CN-PEG750 (**7**)

$(C_9)_2$-CN-SO$_4$Na-PEG350 (**8**)
$(C_9)_2$-CN-SO$_4$Na-PEG550 (**9**)
$(C_9)_2$-CN-SO$_4$Na-PEG750 (**10**)
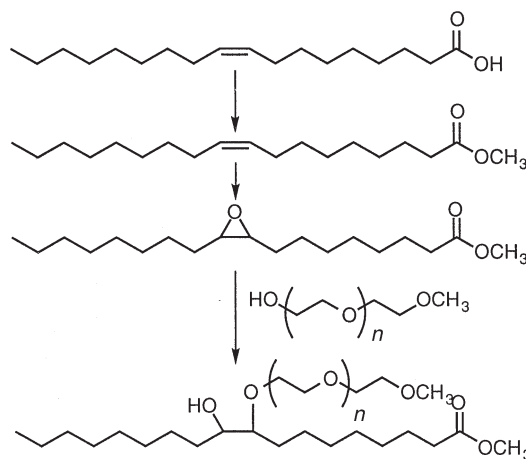
SCHEME 2

surfactants of the same type, but with an ionic sulfate group instead of an alcohol, were also studied (12). The properties of these surfactants [see Scheme 2; structures are from Refs. 11 (left compounds) and 12 (right compounds)] compared to those of our similar surfactants are of interest. Some detailed studies on the surface properties of cationic gemini surfactants (13–16) have also been done.

EXPERIMENTAL PROCEDURES

Materials. Analytical-grade reagents obtained from commercial suppliers were used unless stated otherwise.

Methods. [1]H nuclear magnetic resonance (NMR) spectra were measured at 400 MHz with a Bruker AM-400 spectrometer. The solvent CDCl$_3$ was the reference in all measurements. Only specific protons characteristic of the products are reported, and the ones belonging to the fatty acid skeleton are neglected except for the CH$_3$ group at the end of the chain. Infrared (IR) measurements were recorded on an ATI Mattson Infinity Series Fourier transform IR spectrometer, and the characteristic peaks of the compounds are presented. Equilibrium surface tensions were measured with a SIGMA70 tensiometer (KV) equipped with a Pt-Ir du Noüy ring. The instrument was calibrated against standard pure liquids, and agreement with literature values was typically ±0.1 mN m^{-1}. Double-distilled water was used for all sample preparations. The dynamic surface tensions (DST) were measured using a Lauda MPT2 (maximum bubble pressure tensiometer), which allows measurements to be made with a time resolution from 1 ms to several seconds.

Tall oil fatty acid methyl ester **1**. Tall oil fatty acid (Sylfat 2S containing <2% rosin acids; Arizona Chemical AB, Sardane, Sweden) was esterified with methanol in a semibatch process. Tall oil fatty acid (1500 g) and an esterification catalyst (Fascat 4201, 1.95 g, 0.13 wt%; Altofina Canada Inc., Oakville, Ontario) were charged to a 2-L reaction vessel and heated to 240°C under atmospheric pressure and continuous nitrogen flow. Methanol was pumped in at a rate of approximately 1.3 mL/min through a capillary ending at the bottom near the mechanical stirrer. The reaction was nearly instantaneous and the water formed during reaction boiled

off. After 8 h at 240°C, 460 mL of methanol was totally used and the acid value was <3 mg KOH/g; the mixture was then cooled. Distillation at 195°C (1 mbar) gave the pure methyl ester at a 91% yield. Acid value 1.7 mg KOH/g. Color (Gardner 63): 3.5. ^{1}H NMR (400 MHz, δ): 0.70 (*m*, 3H, –**CH**$_3$), 1.0–1.3 (*m*, 22H, –**CH**$_2$–), 1.40 (*t*, 2H, **CH**$_2$–CH$_2$COOMe), 1.85 (*m*, 2H, –CH=CH–**CH**$_2$–), 2.10 (*t*, 2H, CH$_3$OCOCH$_2$–), 2.60 (*t*, 1H, –CH=CH–**CH**$_2$–CH=CH–), 3.60 (*s*, 3H, **CH**$_3$OCO–), 5.20 (*m*, 3H, –**CH**=CH–). Gas chromatography (GC) (17): methyl ester composition as follows: stearic 1.4%, oleic 31.7%, linoleic 40.4%, C18:2 conjugated 5.4%, pinolenic 8.0%, C18:3 conjugated 2.6%, C20:3 conjugated 1.7%, other methyl esters 7.3%, free fatty acids 1.5%.

Tall oil fatty acid methyl ester monoepoxide **2**. The Ishii–Venturello epoxidation catalyst was prepared as follows: Tungstenic acid (6.8 g, 27.2 mmol) and 30% hydrogen peroxide (24.0 g; 212 mmol) were charged to a 2-L reaction vessel and heated to 60°C in a water bath. After 40 min the mixture had whitened and most of the acid was dissolved. After cooling to room temperature, 40% phosphoric acid (1.96 g; 8 mmol) was added followed by 70% Q-salt ARQUAD 2C-75 (Akzo Nobel Surface Chemistry, Stenungsund, Sweden) (8.2 g, 14 mmol). A white solid, the active catalyst mass, was formed. Tall oil fatty acid methyl ester (592 g, 2.00 mol), **1**, was added, and the mixture was heated to 70°C. Hydrogen peroxide (15%; 544 g; 2.4 mol) was added slowly for 60 min. Mechanical stirring 300 rpm was used. The reaction was exothermic and water cooling was necessary to keep the temperature between 60 and 72°C. When all the hydrogen peroxide was added, a heating mantle was used to keep the reaction at 70°C for another 60 min. After heating was turned off and the mixture cooled down toward room temperature, 200 mL ether and 30 g sodium sulfate were added to improve separation. It was then left overnight. The oily layer was dried over magnesium sulfate, and the ether was evaporated. Yield: 627.5 g crude product; epoxide content (epoxide titration according to Ref. 18): 3.16 meq/g. Residues of catalyst were removed by filtering through silica gel. Reanalysis of the epoxide content gave 3.20 meq/g, which was 99.8% of the theoretical value for pure monoepoxide. Analytically pure compound was obtained by chromatographic purification of the crude product. [Medium-pressure liquid chromatography (MPLC) was performed by Peter Bäckström, KTH, Stockholm. Crude product (30 g) was separated on a 50×200 mm silica gel column using a hexane/ethyl acetate gradient as eluent.] ^{1}H NMR (400 MHz, δ): 2.10 (*t*, 2H, –CH$_3$OCOCH$_2$–), 2.75 (*m*, 2H, –**CH**(O)CH–), 2.90 (*m*, 1H, CH=CH–**CH**$_2$–CH(O)CH), 3.60 (*s*, 3H, **CH**$_3$OCO–), 5.20 (*m*, 1H, –**CH**=CH–). GC (obtained with Sylfat 2S): composition as follows: oleic 8.8%, linoleic 2.6%, C18:2 conjugated 1.8%, pinolenic 0.3%, oleic epoxide 29.5%, linoleic monoepoxide 14.5%, pinolenic monoepoxide 2.0%, C20-monoepoxide 1.2%, other monoepoxides 3.3%, diepoxides 25.4%, triepoxides 3.5%, unidentified 7.1%.

Tall oil fatty acid methyl ester hydroxy monomethyl polyethylene glycol (PEG)-350-ether **3** [(C_9)$_2$-*PEG 350*]. Monomethylated PEG-350 (110.3 g, 0.315 mol) was charged to a carefully

dried reaction flask and heated to 60°C. Boron trifluoride (0.55 g, 0.05 wt% on PEG) was added. Tall oil fatty acid methyl ester monoepoxide (93.8 g, 0.300 mol), **2**, was added dropwise for 30 min, and the mixture was heated to 65°C for another 30 min. No residual epoxide could be detected (18). The product was filtered through a bed of sodium hydrogen carbonate (approx. 20 g) to remove catalyst residues. Analytically pure compound was obtained by chromatographic purification of the crude product (as described above). Yield: 200 g (98%). ^{1}H NMR (400 MHz, δ): 0.70 (*m*, 3H, –**CH**$_3$), 1.00–1.30 (*m*, 22H, –**CH**$_2$–), 1.40 (*m*, 4H, –**CH**$_2$–**CH**$_2$–COOMe), 2.08 (*t*, *J* = 7 Hz, 2H, –**CH**$_2$–COOMe), 3.17 (*s*, 3H, –O**CH**$_3$), 3.30–3.50 (*m*, 32H, O–**CH**$_2$**CH**$_2$–O), 3.60 (*s*, 3H, **CH**$_3$OCO–), 4.00 (*m*, 2H, C–**CH**(OR)–C); IR: C–O ether 948 and 1113 cm^{-1}, C(=O)O–C 1250 cm^{-1}, –CH$_3$ 1350 cm^{-1}, O–H 1400 and 3489 cm^{-1}, C–H alkane 1459 and 2873 cm^{-1}, C=O ester 1738 cm^{-1}, O–CH$_3$ 2820 cm^{-1}. Cloud point: 15°C (1% in water). Draves wetting: 45 s. Surface tension: 32.8 mN/m.

Tall oil fatty acid methyl ester hydroxy monomethyl-PEG 550-ether 4 [(C$_9$)$_2$-PEG 550]. Compound **4** was prepared from epoxide **2** (62.5 g, 0.20 mol) in a manner identical to the preparation of compound **3** using monomethylated PEG-550 (115.5 g, 0.21 mol) as the hydrophile. Analytically pure compound was obtained by chromatographic purification of the crude product (as described above). Yield: 172 g (97%). ^{1}H NMR (400 MHz, δ): 0.70 (*m*, 3H, –**CH**$_3$), 1.00–1.30 (*m*, 22H, –**CH**$_2$–), 1.40 (*m*, 4H, –**CH**$_2$–COR), 2.08 (*t*, *J* = 7 Hz, 2H, –**CH**$_2$–COOMe), 3.17 (*s*, 3H, –O**CH**$_3$), 3.30–3.50 (*m*, 48H, O–**CH**$_2$**CH**$_2$–O), 3.60 (*s*, 3H, **CH**$_3$OCO–), 4.00 [*m*, 2H, C–**CH**(OR)–C]; IR: C–O ether 948 and 1109 cm^{-1}, C(=O)OC 1250 cm^{-1}, –CH$_3$ 1350 cm^{-1}, O–H 1400 and 3491 cm^{-1}, C–H alkane 1458 and 2873 cm^{-1}, C=O ester 1758 cm^{-1}, O–CH$_3$ 2820 cm^{-1}. Cloud point: 46°C (1% in water). Draves wetting: 65 s. Surface tension: 33.4 mN/m.

Tall oil fatty acid methyl ester hydroxy monomethyl-PEG 750-ether 5 [(C$_9$)$_2$-PEG 750]. Compound **5** was prepared from epoxide **2** (50 g, 0.16 mol) in a manner identical to the preparation of compound **3** using monomethylated PEG-750 (126 g, 0.168 mol) as the hydrophile. Analytically pure compound was obtained by chromatographic purification of the crude product (as described above). Yield: 170 g (97%). ^{1}H NMR (400 MHz, δ): 0.70 (*m*, 3H, –**CH**$_3$), 1.00–1.30 (*m*, 22H, –**CH**$_2$–), 1.40 (*m*, 4H, –**CH**$_2$–COR), 2.08 (*t*, *J* = 7 Hz, 2H, –**CH**$_2$–COOMe), 3.17 (*s*, 3H, –O**CH**$_3$), 3.30–3.50 (*m*, 68H, O–**CH**$_2$**CH**$_2$–O), 3.60 (*s*, 3H, **CH**$_3$OCO–), 4.00 (*m*, 2H, C–**CH**(OR)–C); IR: C–O ether 949 and 1106 cm^{-1}, C(=O)O–C 1250 cm^{-1}, –CH$_3$ 1350 cm^{-1}, O–H 1400 and 3508 cm^{-1}, C–H alkane 1460 and 2873 cm^{-1}, C=O ester 1738 cm^{-1}, O–CH$_3$ 2820 cm^{-1}. Cloud point: 63°C (1% in water). Draves wetting: 213 s. Surface tension: 38.0 mN/m.

Tensiometry. A detailed description of the instrument and measurement procedure can be found elsewhere (19). The calibration was checked using double-distilled water. It is important to state that the surface tension of the calibrant was constant over the time range of 0.01–1 s. The effective surface age, *t* (effective adsorption time), from the bubble surface lifetime was calculated as described (20). All the tensiometry measurements were carried out with freshly made solutions at 20.0 ± 0.1°C.

Reflectometry. A laser giving a plane-polarized light beam was used as the light source. In a typical reflectometer, monochromatic light (He-Ne laser, 633 nm) is linearly polarized and passes through a 45° glass prism. This beam arrives at the interface with an angle of incidence close to the Brewster angle (θ = arctan n_2/n_1) for the solvent–substrate interface. In our case a silicon wafer was used as substrate and water as solvent (nSi = 3.8 and nH$_2$O = 1.33); the angle of incidence was around 71°. At this angle, any substance adsorbed at the silicon–water interface that has a refractive index different from the two media will change the reflectance. The adsorbed amount was calculated from the equation

$$\Gamma = Q\frac{\Delta S}{S_0} \qquad [1]$$

where Γ is the adsorbed amount (mg/m^2), Q is the sensitivity factor (mg/m^2), ΔS is the output signal attributable to adsorption and S_0 is the output signal at $t = 0$.

Polished silicon wafers, thermally oxidized to produce a SiO$_2$ layer thickness of ~100 nm and then cut into slices with a width of 12.5 mm, were used. The slides were cleaned in a mixture of NH$_4$OH, H$_2$O$_2$, and H$_2$O followed by cleaning in a mixture of HCl, H$_2$O$_2$, and H$_2$O, and then stored in ethanol until used. Just before being placed in the reflectometer cuvette, the slides were cleaned in Milli-Q water.

To obtain a hydrophobic surface, the silica plate was modified according to standard methods by dimethyldichlorosilane (DDS). DDS reacts with the silanol groups of the surface, and the resulting –Si(CH$_3$)$_2$ groups are bound covalently to the silicon oxide film, forming a top layer of densely packed methyl groups (21).

Turbidimetry, surface tension, and reflectometry samples were prepared using double-distilled water as solvent. All solutions were clear and homogeneous at the measurement temperature, 20°C.

RESULTS AND DISCUSSION

Synthesis. The procedure that was developed for the preparation of the new type of nonionic surfactant is industrially applicable, since there are only three neat reaction steps with no solvents used and with high yields. Total yield was 89%. Some factors regarding the synthesis, as presented in Scheme 1, are important to observe. In step 1 the temperature is critical. Below 220°C the reaction is very slow, and above 250°C the fatty acid polymerizes and will form dark-colored by-products. Also, the catalyst induces a darkening of the product in concentrations above 0.1 wt%. A reaction temperature of 240°C and 0.13 wt% catalyst gave a reasonably short total reaction time and light-colored products. According to the results of a Karl Fischer titration performed during the reaction, the distillate consisted of 90% water at the beginning of the process and of 5–10% at the

end of the reaction time (the rest being excess or unreacted methanol). Thus, at this temperature the injected methanol reacted almost immediately with fatty acid in the presence of the catalyst. The water formed boiled off from the mixture together with unreacted methanol, meaning that the methanol content in the distillate increased as the esterification proceeded. The high reaction rate means that only relatively small amounts of excess methanol need to be used in the reaction. In step 2 the excess of H_2O_2 was critical and should be about 20 mol% in order to obtain a high yield of monoepoxide. With 10 mol% excess, the reaction was not completed, and with 30% excess, a large amount of diepoxide was formed. In step 3, the order of addition was very important. When BF_3 was added to the epoxide instead of the alcohol, no addition product was formed. The corresponding ketone was probably formed from the epoxide. In order to remove the hydrophobic by-products and residual starting material, the surfactants were purified by MPLC as described above before the characterization or the analysis of surface chemistry properties were performed.

Clouding behavior. One important property of surfactants in aqueous solution is the separation into two phases above the cloud point temperature, a phenomenon that is well known for oxyethylene-based surfactants (C_nE_m, where n is the number of hydrophobic carbons and m is the number of ethylene oxide units). Cloud point measurements were performed by visual observation in glass tubes. After heating the samples above the clouding temperature, the cloud point was taken as the temperature at which the last visible sign of opalescence disappeared on cooling. All measurements were reproducible within ±2°C even when the temperature was increased or decreased relatively quickly (i.e., several degrees per minute). Cloud point data for the surfactants

$(C_9)_2$-PEG350 (**3**), $(C_9)_2$-PEG550 (**4**), and $(C_9)_2$-PEG750 (**5**) are presented in Figure 1 as a function of concentration.

The demixing curves exhibit the same features as those of low molecular weight nonionic surfactants (21,22), i.e., the lower critical solution temperature (LCST) increases with the length of the hydrophilic chain. The LCST obtained for the two surfactants are, of course, lower than those for a conventional nonionic surfactant with a single hydrophobic chain of the same length (i.e., 9–10 carbon) and with the same number of oxyethylene groups, for instance, $C_{10}E_8$ with a cloud point about 85°C (21). A comparison of the cloud points of our branched surfactants with those of previously known, straight-chained derivatives (Ref. 23; see Fig. 2) illustrates that our branched surfactants have much lower cloud points than their straight-chain equivalents. This shows that the twin-tailed surfactant is more hydrophobic than its straight-chain counterpart.

A comparison of the cloud points of compounds **4** and **5** (63 and 84°C, respectively) with those of the near-identical hydrophobe twin-chained compounds **6** and **7** (63 and 74°C, respectively, from Ref. 11) also seems to suggest that exchanging the methyl ester functionality into a nitrile functionality will make the surfactant slightly more hydrophobic as a whole.

Equilibrium surface tensions. For both surfactants investigated, the variation of the surface tension (γ) with the surfactant concentration (C) and the surface excess concentration (Γ) were determined in a semilogarithmic representation, as shown in Figure 3. The equilibrium time was at least 15 min for each concentration. All measurements were made multiple times for each different concentration; thus, the surface tension given is the average value of all measurements. The plot of γ vs. log C shows a break at a concentration corresponding to the critical micelle concentration (CMC). The CMC values are 2.0, 1.0, and 0.4 mM for $(C_9)_2$-PEG350, $(C_9)_2$-PEG550, and $(C_9)_2$-PEG750, respectively.
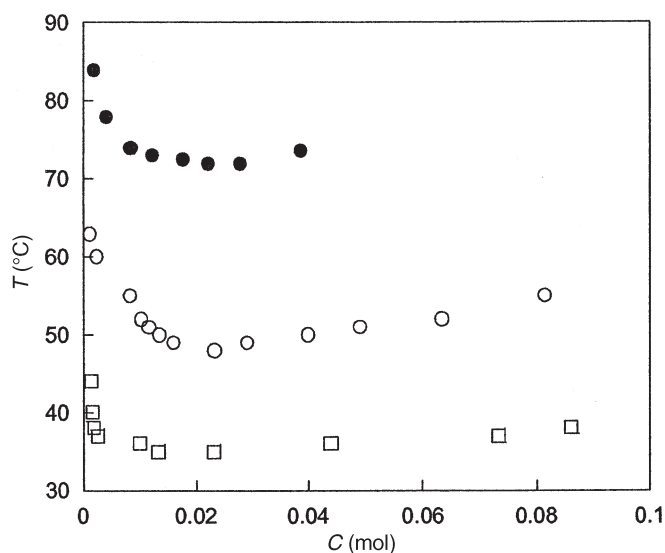

FIG. 1. Cloud points for tall oil fatty acid methyl ester hydroxy monomethyl-PEG 350-ether [$(C_9)_2$-PEG350] (□), tall oil fatty acid methyl ester hydroxy monomethyl-PEG 550-ether [$(C_9)_2$-PEG550] (○), and tall oil fatty acid methyl ester hydroxy monomethyl-PEG 750-ether [$(C_9)_2$-PEG750] (●). Concentration (C) of surfactant in moles vs. temperature (T) in degrees Celsius.
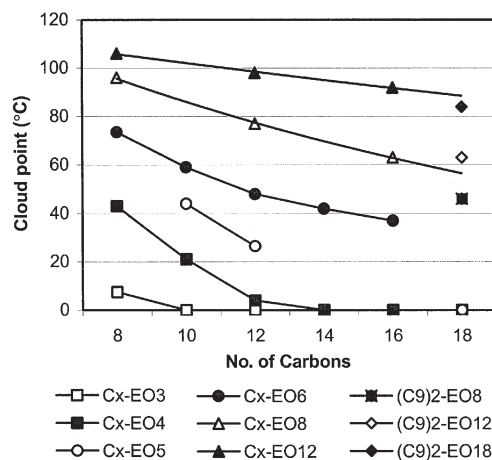

FIG. 2. A comparison of cloud points for $(C_9)_2$-PEG350, $(C_9)_2$-PEG550, and $(C_9)_2$-PEG750 and their straight-chained equivalents. Number of hydrophobic carbons (C_x) for a set number of ethylene oxide (EO) units of surfactant vs. the cloud point (T) in degrees Celsius. For other abbreviations see Figure 1.

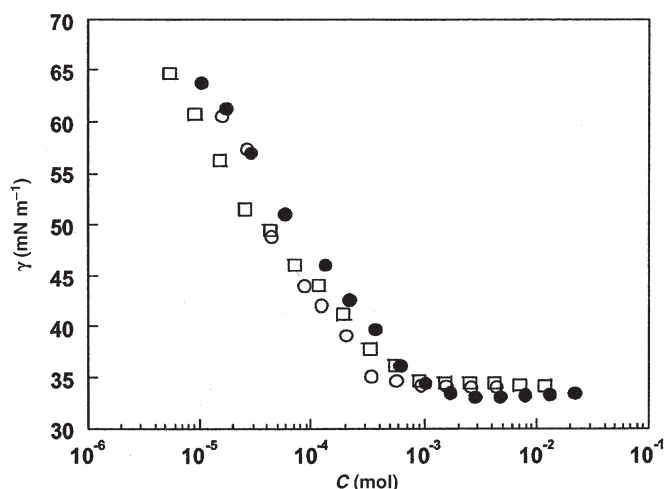**FIG. 3.** Equilibrium surface tensions for solutions of $(C_9)_2$-PEG350 (●),$(C_9)_2$-PEG550 (○), and $(C_9)_2$-PEG750 (□) at 20°C. Concentration (C) of surfactant in moles vs. surface tension (γ) in dynes. For abbreviations see Figure 1.
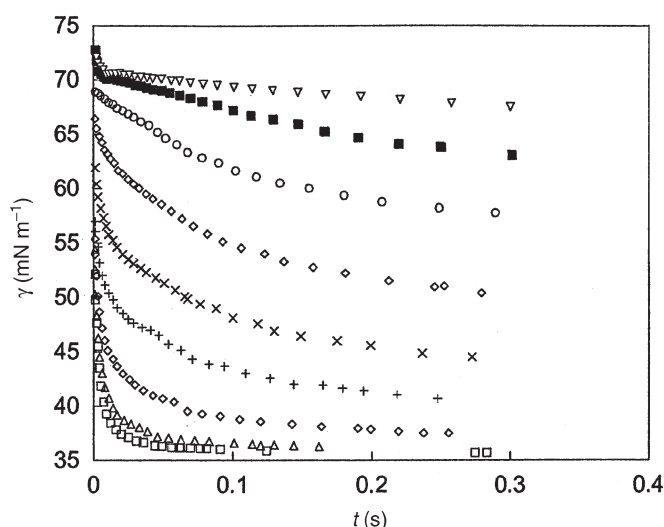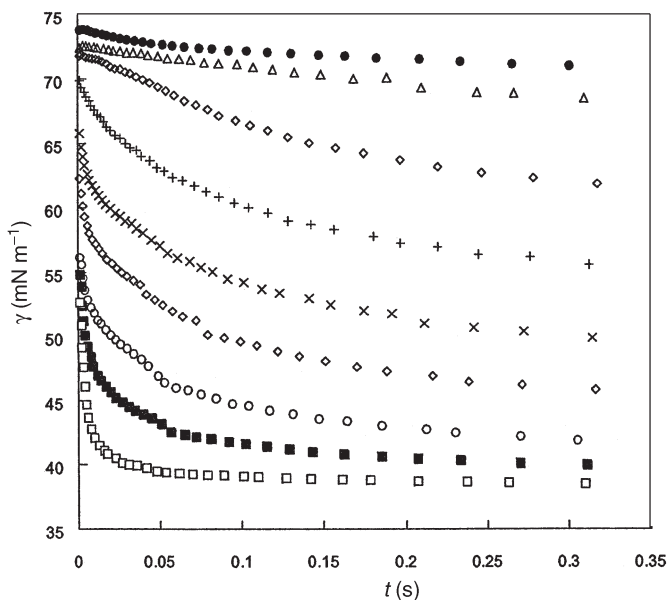

FIG. 4. Dynamic surface tension of $(C_9)_2$-PEG350. Decay time (t) in seconds vs. surface tension (γ) in dynes. (In percentages) (□) 1.45; (△) 0.87; (◇) 0.52; (+) 0.31; (×) 0.18; (◊) 0.11; (○) 0.06; (■) 0.04; (▽) 0.02. For other abbreviation see Figure 1.

These are much higher values than those of the straight-chained equivalents, which is to be expected. The previously reported (11), and very structurally similar, nitrile-based compounds **6** and **7** are given CMC values of 0.20 and 0.40 mM, respectively. The lower CMC value of compound **6** compared to compound **4** is of interest. It would appear as if the slightly higher hydrophobicity of **4** somewhat facilitated micellar formation. The surface tension, γ_{CMC}, is in approximately the same range for all of these compounds.

According to Gibbs law applied to equilibrium systems, the adsorption of surfactant to the gas–liquid interface leads to a reduction in the surface tension of the solution. The surface excess concentration Γ and the surface area a of the surfactant were calculated using the Gibbs equation:

$$\Gamma = -\frac{1}{2.3nRT}\left(\frac{d\gamma}{d\log C}\right)_T = \frac{1}{aN_A} \quad [2]$$

where R is the gas constant, T the Kelvin temperature, and n a constant that depends on the number of species constituting the surfactant and that are adsorbed at the interface. For neutral molecules, $n = 1$.

The head group areas were calculated and values of about 45 Å^2 were obtained. These values are lower than that of a nonionic surfactant with a single hydrophobic chain and a polyoxyethylene head group (for instance, $C_{12}E_8$ has a head group area of about 63 Å^2), even though they contain two hydrophobic chains. This trend is as expected since the hydrophobic group is larger. These values are, surprisingly, also lower than those of compounds **6** and **7** (11), suggesting that the monolayer formed is relatively closely packed. Note, however, that the effect of PEG on the CMC is rather small.

DST. DST is an important property of surfactant solutions, and a number of different models have been proposed to account for the decay. Elwing *et al.* (20) provide an excellent background. DST measurements were made at

concentrations between 0.1 and 10 times the CMC for all surfactants. Examples of the γ (t) decays are shown for solutions of $(C_9)_2$-PEG350, $(C_9)_2$-PEG550, and $(C_9)_2$-PEG750, respectively (Fig. 4–6). These data are representative of the effect of concentration on the DST. For the highest concentrations at the shortest possible measuring time (2 ms), the tensions were already lower than the solvent value, γ_0, showing the rapid process of adsorption. At lower concentrations, on the other hand, the decay of DST showed a progressive adsorption process. Despite repeated attempts, it was not possible to obtain data at surface ages greater than 0.4 s for different concentrations.

FIG. 5. Dynamic surface tension of $(C_9)_2$-PEG550. Decay time (t) in seconds vs. surface tension (γ) in dynes. (In percentages) (□) 0.632; (■) 0.379; (○) 0.227; (◇) 0.136; (×) 0.081; (+) 0.049; (◊) 0.029; (△) 0.017; (●) 0.010. For other abbreviation see Figure 1.
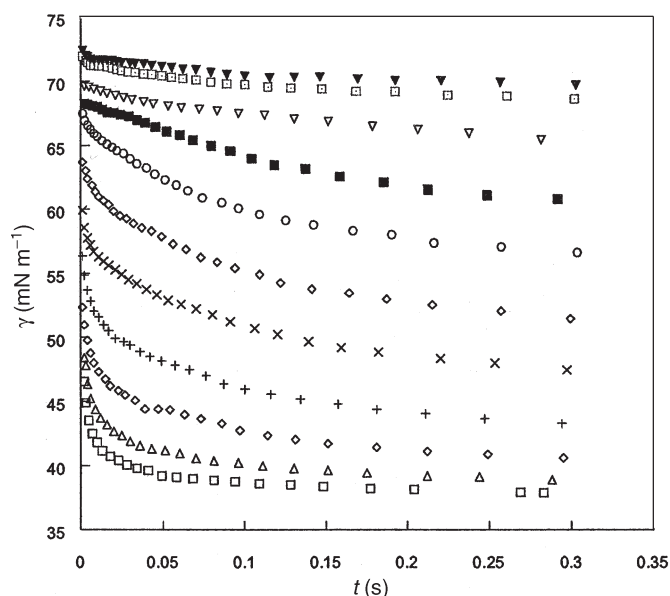
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