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Interaction of the Acid Soap of Triethanolamine Stearate and Stearic Acid with Water

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Stearic acid and triethanolamine (TEA) in a molar ratio of 2:1 were mixed in aqueous solution at 80 °C and subsequently cooled to ambient temperature. The structural evolution of the resultant sample during storage was characterized by using light microscopy, Cryo-SEM, differential scanning calorimetery, pH, infrared spectroscopy, elemental analysis, and simultaneous small and wide-angle X-ray diffraction. It was found that a lamellar liquid crystalline phase was formed when stearic acid and TEA solution were mixed at 80 °C and multilamellar spheres of a few microns diameter were formed initially after cooling. A hydrolysis reaction (i.e., the reverse reaction of neutralization between stearic acid and TEA) occurred thereafter that caused the breakdown of the lamellar gel phase and the formation of platelet stearic acid crystals. Three polymorphs of stearic acid (defined following previous work as the A, C, and E forms) were formed as the result of hydrolysis reaction, which gave rise to a strong optically pearlescent appearance.

1. Introduction

The interactions and phase behavior of alkaline soaps and acid soaps of long chain fatty acids in aqueous solution have been the subject of many studies.[1−4] These systems are also widely used in many household products such as cosmetics and personal washes.[5,6] Soaps and acid soaps neutralized with amine bases have not received as much attention even though they are used in many cases as alternatives to alkaline bases.[6−9] Recently the current authors reported a phase behavior study on the binary system of stearic acid and triethanolamine stearate and discovered significant differences compared with the binary systems of alkaline soap and stearic acid.[10] For example, a 2:1 acid soap complex was identified from the TEA binary system. The melting temperatures of the TEA soap and the acid soap were found to be significantly lower than those of the corresponding alkaline soap and acid soap due to the significantly larger size of the TEA cation. Earlier work by Warnheim and Jonsson[7,8] showed that the phase behavior of TEA stearate and water was significantly different from that of the alkaline soap and water due to the difference in cation size. A large undetermined area in the phase diagrams at low surfactant concentrations, up to 30%, was reported by those papers. The aim of this paper is thus to extend the work of the binary system into the aqueous environment and investigate how the TEA acid soap interacts with water at an acid soap concentration of 20%, which is typically used in skin care products.

Concentrated aqueous solutions comprised of stearic acid partially neutralized with TEA were prepared. The degree of neutralization was chosen to be 33%, corresponding to the 2:1 acid soap complex ratio as reported in the literature.[10] Microscopy, differential scanning calorimetry, infrared spectroscopy, pH measurement, and X-ray diffraction were used to characterize the structural changes of the sample during and after preparation. The experimental results provide new understanding of amine based acid soap interaction with water, the neutralization and hydrolysis between weak acid, stearic acid, and weak base, TEA aqueous solution. It also demonstrates a new method of polymorphism formation of stearic acid crystal in aqueous solution.

2. Experimental Method

2.1. Materials. Stearic acid and triethanolamine (TEA) were provided by Fisher Scientific. Stearic acid and TEA purities were 98% and 99%, respectively. Deionized water was used in the sample preparation. The neutralization of stearic acid was calculated by using the molar ratio of stearic acid to TEA. The concentration of water and surfactants was calculated in weight percentage.

2.2. Sample Preparation. Stearic acid powder was melted at 80 °C. TEA was dissolved in water and the solution was heated to 80 °C. The two liquids were then mixed together at 80 °C for 10 min with use of a magnetic stirrer. The mixture was then cooled at room temperature (20 °C). The sample was stirred with a spatula as the sample thickened during cooling. The neutralization was fixed at 33% and the water content was fixed at 80%. This sample will be referred to as the unseparated sample. Characterization of the unseparated sample was performed as a function of time after cooling.

After 3 months at room temperature, unseparated sample, diluted 5 times with deionized water, was separated, using a centrifuge (Sorvall Instrument RC5C for 30 min at 8000 rpm), into a solid layer and a liquid layer. The solid layer was washed with deionized water repeatedly until the pH of the washed liquid was about 7. The separated solid was dried in vacuum at room temperature. This sample will be referred to as the separated solid.

2.3. Optical Microscopy. The sample was placed on an optical glass slide, covered with a cover slip, and monitored by using transmitted bright field or polarized light. At 80 °C a Linkam hot stage was used to control the sample temperature. The sample was taken at 80 °C and placed on the hot stage. Images were taken immediately.

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2.4. Cryo-Scanning Electron Microscopy (SEM). Samples were prepared for Cryo-SEM by sub-sampling ca. 4 mm × 4 mm × 8 mm pieces at room temperature, mounting them in a 6 mm diameter drilled depression on an SEM stub using Tissue TEK, and plunging them into nitrogen slush. After transferring to an Oxford Instruments CP2000 preparation chamber the samples were warmed to − 95 °C, fractured, and deep etched for 5 min. The temperature was allowed to cool to −110 °C. Following metal coating (6×10^{-1} mBar Ar, 6 mA, Au/Pd, 20 s) the samples were transferred in vacuum to a JEOL 6301 FESEM fitted with a Cressington cold stage (−150 °C) for examination.

2.5. Thermal Analysis. Unseparated sample (30 to 50 mg) was sealed inside a water-tight stainless steel pan. For separated sample 10 to 20 mg was used for DSC analysis. Differential scanning calorimeters (Perkin-Elmer Diamond) were used to analyze samples at two scanning rates of 1 and 10 deg/min. The temperature range used was 10 to 90 °C.

Peak temperatures and enthalpies were measured from the DSC traces by using the partial areas method of the Perkin-Elmer Thermal Analysis Pyris software and by fitting multiple Gaussian peaks to the profiles.

2.6. pH Measurement. A pH meter, Hanna pH 302, and a flat double junction pH/reference electrode (from VWR Cat. No. 662-1805), calibrated with standard buffer solution (pH 7 and 10), were used to measure the pH. Temperature range of the pH meter and electrode are from −9.9 to 120 °C and from 10 to 100 °C, respectively. A thermocouple connected to the pH meter was inserted inside the sample for automatic temperature compensation.

2.7. Small- and Wide-Angle X-ray Scattering (SAXS/WAXS). X-ray scattering was used to provide the structural states of the samples as a function of neutralization and temperature. X-ray experiments were performed on station 16.1 at the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory in the United Kingdom. The details of the experimental setup have been described elsewhere.[1,10] A simultaneous small-angle/wide-angle X-ray scattering (SAXS/WAXS) static (exposure time 60 s) was taken for all the samples at ambient temperature. The data at 80 °C were obtained by heating the sample inside a sealed aluminum DSC pan with one mica window[1] in a modified Linkam hot stage in a simultaneous in situ SAXS/WAXS/DSC run at 10 deg/min from 20 to 120 °C with 20 s exposures.

2.8. Infrared Spectroscopy. The experiments were carried out with a biorad FTS 6000 FTIR spectrometer. The samples were measured with a diamond ATR "golden gate" (Geasby Specac UK. Ltd). Spectra were taken at a resolution of 2 cm^{-1} and each spectrum consisted of 256 scans co-added and ratioed against an air background spectrum. A series of background spectra were collected before each experiment according to the temperatures at which measurements were to be made. The correct background was then chosen to ratio against the sample spectra according to the temperature. In the case of solutions a pure water spectrum was subtracted where necessary.

2.9. Elemental Analysis. Elemental analysis was carried out by Elemental Microanalysis Ltd, UK, with CE Instruments (Carlo Erba) Model 1110.

3. Results

3.1. Characterization of Unseparated Sample at 80 °C. After the 80 °C molten stearic acid was mixed into the 80 °C TEA solution, a viscous and gel-like mixture was formed. Microscopy of the sample at 80 °C (Figure 1) shows a weak partially oriented birefringence and no droplets. The SAXS profile of the sample at 80 °C (Figure 2) shows multiple diffraction peaks of a lamellar liquid crystal phase with a lamellar spacing of 174 Å (WAXS showed molten unoriented chains). The pH of the TEA solution at 80 °C was 9.3. After mixing with the molten stearic acid the pH of the sample decreased to 7.2.

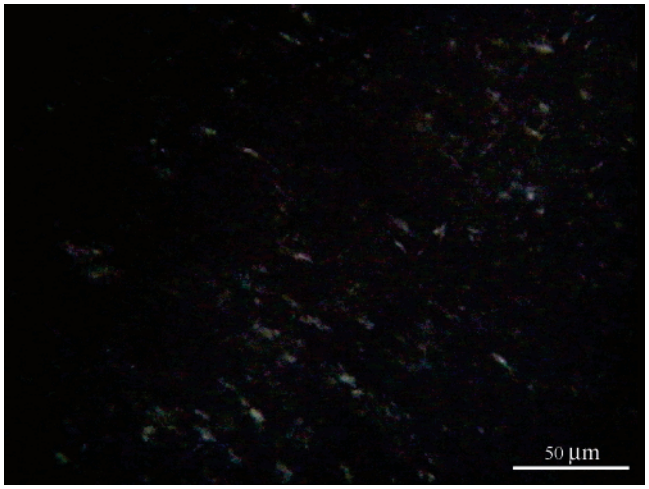


Figure 1. Polarized light micrograph of the unseparated sample at 80 °C.

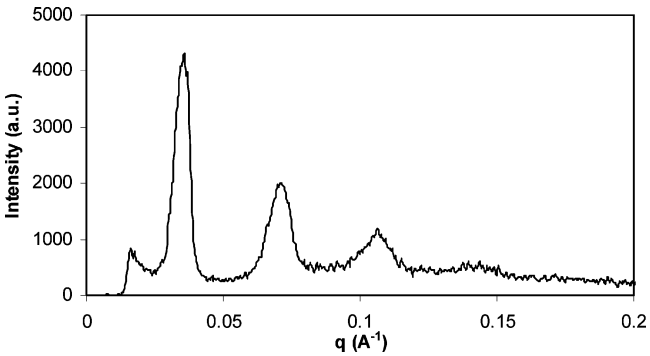


Figure 2. SAXS profile of the unseparated sample at 80 °C.

3.2. Structural Evolution of the Unseparated Sample at Ambient Temperature. On cooling to room temperature the unseparated sample was characterized with DSC, microscopy, Cryo-SEM, X-ray diffraction, IR, and pH as a function of storage time at ambient temperature.

The overall visual appearance of the bulk sample changed with time. To begin with it was a translucent gel, over a few hours it turned white. Solid crystals with a pearly appearance became apparent after 5 h. The sample then gradually separated into two phases, and after a few weeks a clearly separate liquid phase and a solid-pearly crystalline phase were observed.

3.2.1. Microscopy. The 0 h highly viscous sample under polarized light shows Maltese crosses and aligned weak birefrigence (see Figure 3a). Highly birefringent regions have appeared after 3 h (Figure 3b) and continue to appear before 24 h (Figure 3c). Figure 4 shows bright field micrographs for the same samples at zero hours, Figure 4a, and four weeks, Figure 4b, after preparation. It was seen that the fresh sample contained many small spheres, a few microns in diameter, and no solid crystals in the sample. The sample after four weeks contains many large solid crystals with well-defined edges.

The Cryo-SEM micrographs are shown in Figure 5. The image of the sample immediately after cooling shows spherical balls present with diameters in the range of a few microns. The

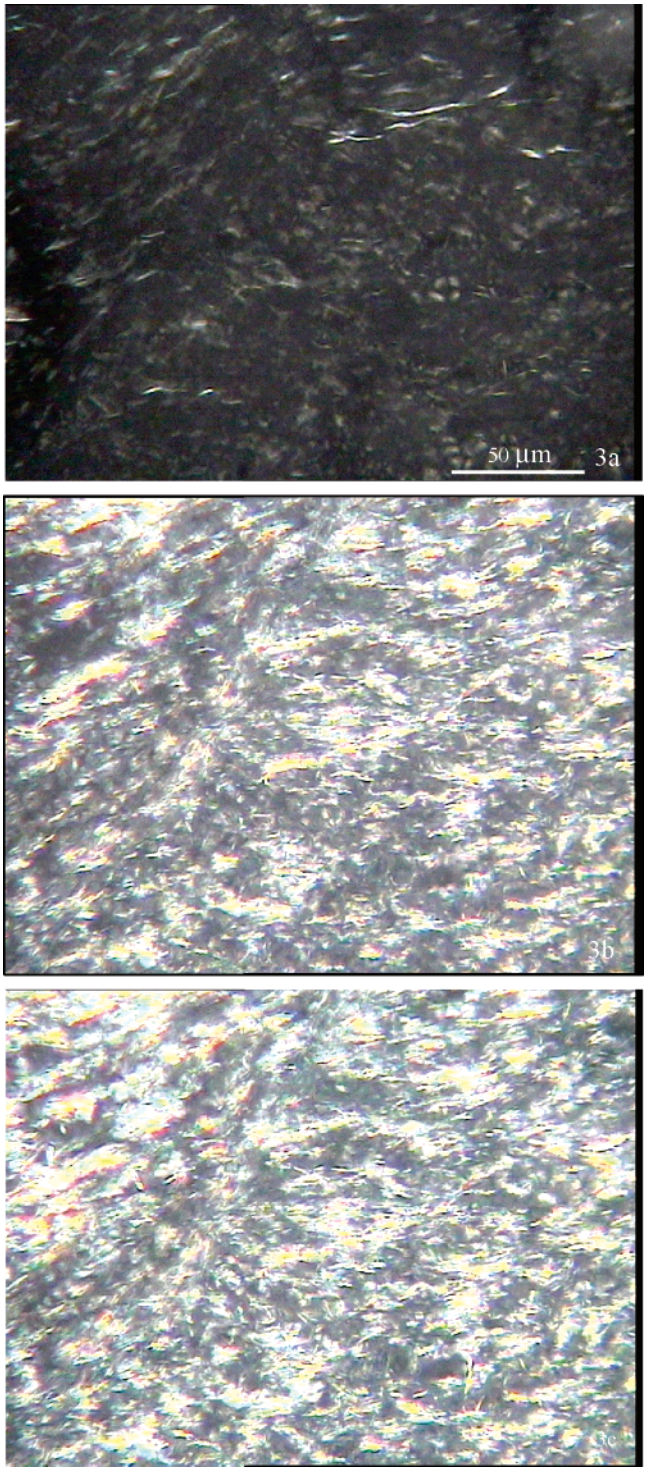


Figure 3. Polarized light micrographs of the unseparated sample at different storage times at room temperature: (a) 0, (b) 3, and (c) 24 h.

image also shows that the shell of the ball contained multiple layers (Figure 5d). After 5 h the microstructure had evolved so that a few platelets were present. The dimensions of the platelets were very similar to those observed by light microscopy. More platelets developed with storage time and at about 22 h, Figure 5c, the platelet structure is the dominant feature and the balls have almost disappeared.

3.2.2. Thermal Analysis. The DSC heating curves of the unseparated sample at different storage times after preparation are shown in Figure 6. A single melting peak at 67.7 °C, onset temperature of ca. 58 °C, was obtained from the sample prepared

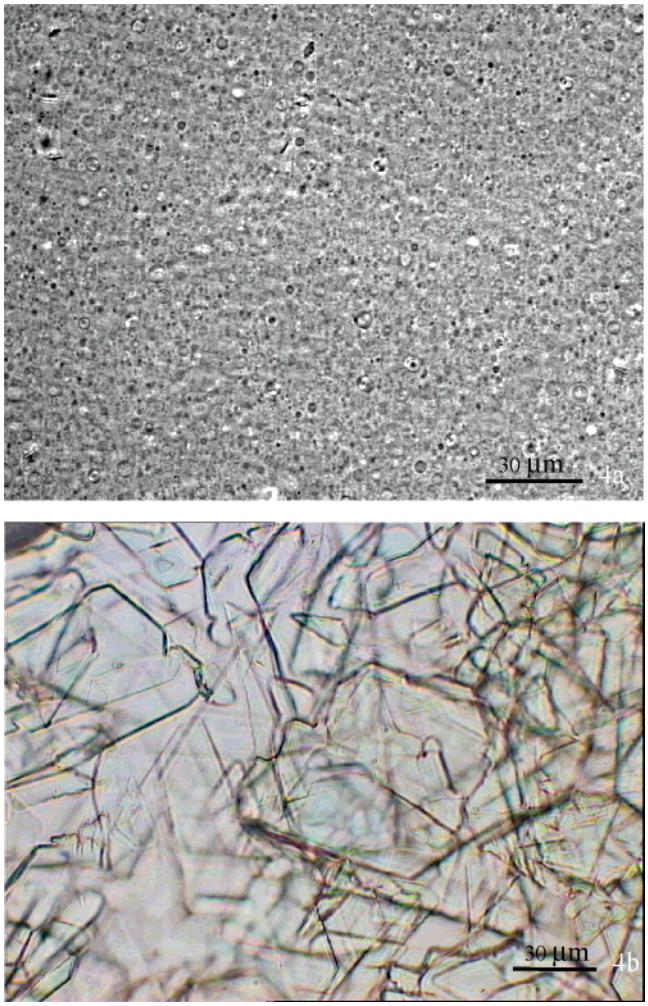


Figure 4. Bright field light micrographs of the unseparated sample at different storage times at room temperature: (a) 0 h and (b) 4 weeks.

and stored at ambient temperature for 2 h. Its enthalpy was 14 J/g. The melting curve for the sample stored 5 h at ambient temperature showed a shoulder at around 56 °C in addition to the main peak at 67.7 °C. The enthalpy of the peak at 67.7 °C remained constant. The enthalpy of the shoulder peak increased and the onset temperature decreased with increasing the storage time. It became stable after 24 h and reached a melting enthalpy of 14 J/g. The enthalpy and melting point of the main peak did not vary as a function of preparation time.

All the cooling curves (Figure 7) of the samples showed a major transition at approximately 55 °C. The enthalpies of the transition at 55 °C were very similar at 14J/g for all the different storage times. Sometimes an exothermic peak was observed at approximately 10 °C, with the size and peak temperature being small but variable. The variation of peak sizes and positions are random with regard to the storage time and sample mass.

The reheating behaviors immediately after cooling to room temperature of the sample with different storage times showed only the one main peak at 67.7 °C (a small peak may appear at a lower temperature if the peak at around 10 °C in the cooling curve occurs).

3.2.3. pH at Various Storage Times. The pH of the unseparated sample increased slightly from 7.2 observed at 80 °C to 7.5 immediately after cooling. It increased steadily with storage time and reached a constant value of 9.1 after a few days.

3.2.4. X-ray Diffraction at Various Storage Times. To understand the crystallization behavior during storage time

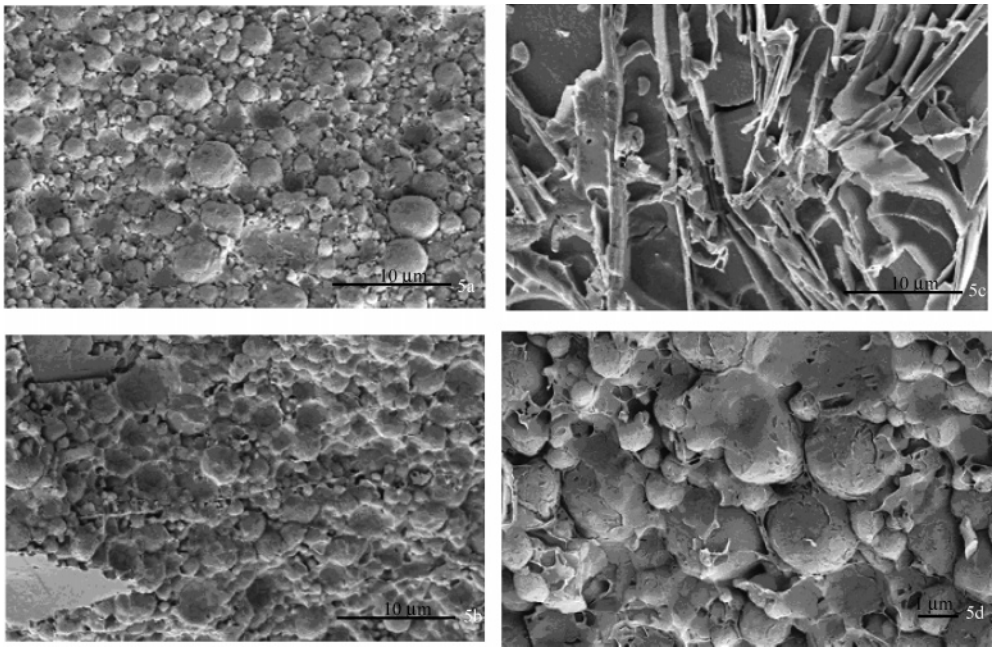


Figure 5. Cryo-SEM images of the unsepared sample at different storage times at room temperature: (a) 0, (b) 5, (c) 24, and (d) 0 h (higher magnification).

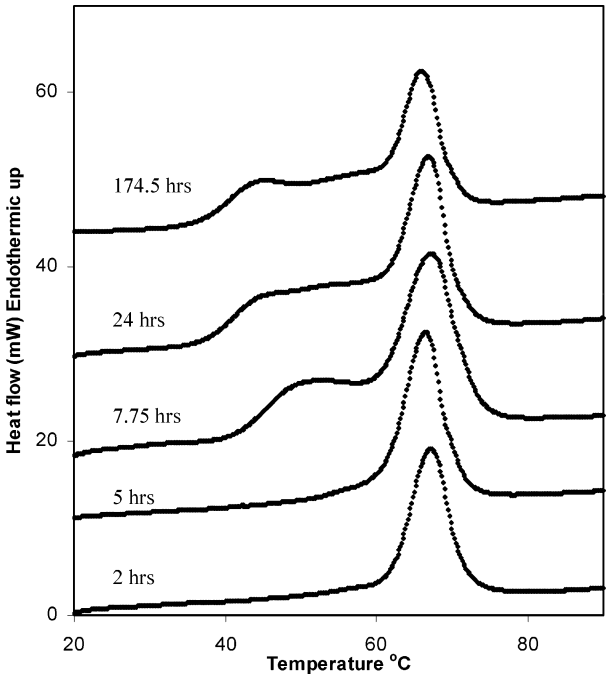


Figure 6. DSC heating curves of the unseparated sample at different storage times at room temperature, the data were not normalized by weight. Heating rate = 10 °C/min.

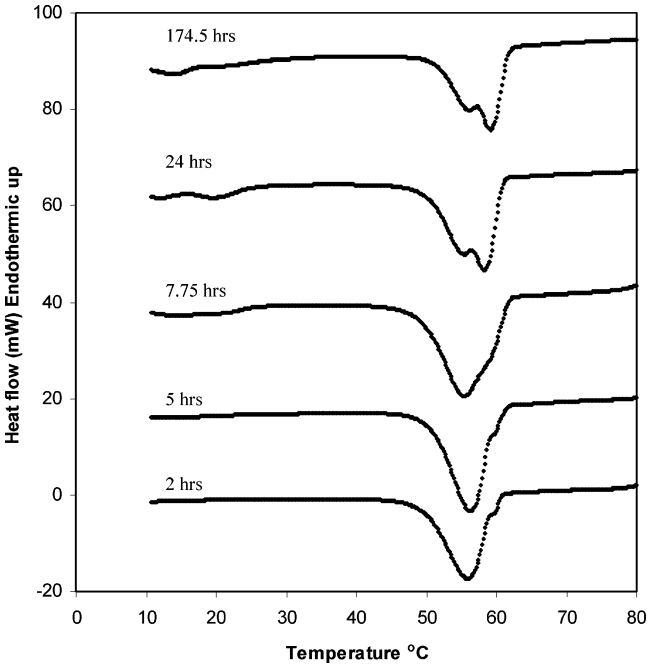


Figure 7. DSC cooling curves of the unseparated sample at different storage times at room temperature; the data were not normalized by weight. Cooling rate = 10 deg/min.

SAXS and WAXS were performed at different time intervals after preparation of the unseparated sample. The SAXS curves are plotted in Figure 8.

The SAXS results of the freshly prepared sample showed multiple ordered diffraction peaks representing a swollen lamellar phase. The corresponding WAXS data only showed a sharp peak at 4.2 Å. These results indicate that the lamellar structure of the freshly prepared sample was a gel phase at room temperature (below the hydrocarbon chain melting point[1,11]). The lamellar spacing of the gel phase was 286 Å. There were no diffraction peaks observed for crystalline stearic acid, which has a bilayer spacing in the range 40 to 50 Å depending on the crystal polymorphs present.[4,12−18]

After 4 h of storage the lamellar phase was still present with a slightly shorter long spacing of 273 Å and also a new peak at 40 Å appeared. At 18 h there was a very broad peak centered around 90 Å and a very strong peak at 40 Å. At 22 h there was only a strong peak at 40 Å. The SAXS profile for the sample after 99 days shows a sharp peak at 40 Å, a small peak at 44.7 Å, and a third weak peak at 46.6 Å.

3.2.5. IR Spectroscopy. The IR spectrum of the aged sample (99 days) was measured and is presented after the subtraction of a water spectrum (Figure 9). It shows the main region of interest—the strongest band is observed at 685/6 cm^{-1} with some further intensity at lower frequency.

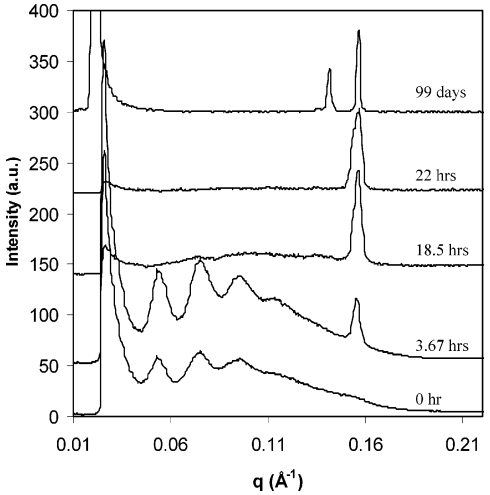


Figure 8. SAXS profile of the unseparated sample at different storage times at room temperature.

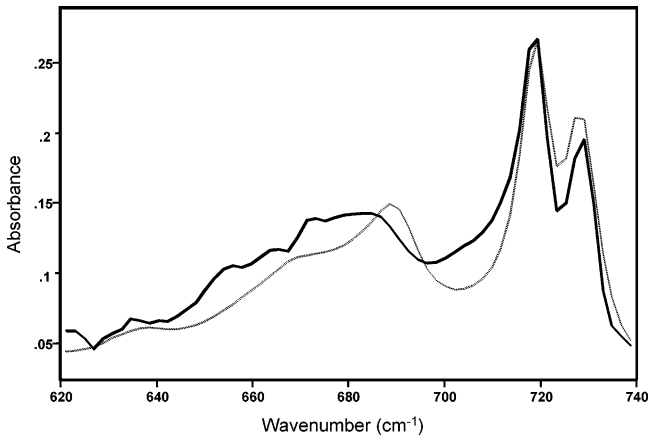


Figure 9. IR of the unseparated sample stored for 99 days with the spectrum of water subtracted out (solid line) and C form stearic acid (dashed line) at room temperature.

TABLE 1: Elemental Analysis of Separated Solid

crystal	C (%)	H (%)	O (%)	N (%)
stearic acid (from Fisher Scientific)	76.1	13.0	10.9	0
separated solid	76.2	13.0	10.7	0.04
stearic acid (theoretical value)	76.0	12.8	11.2	0
33% neutralized stearic acid/ TEA (theoretical value)	71.9	12.4	14.4	1.40

3.3. Characterization of the Separated Solid. The solid precipitated in the stored unseparated sample (3 months) was separated from the liquid layer with a centrifuge. The separated solid was washed with deionized water until the pH value of the washed water was close to neutral. The solid was then dried in a vacuum oven at room temperature.

3.3.1. Elemental Analysis. The elemental compositions (carbon, hydrogen, oxygen, and nitrogen) in the separated solid and an aliquot of the stearic acid used to prepare the sample were measured and the results are shown in Table 1. The theoretical elemental compositions of pure stearic acid and 33% neutralized stearic acid with TEA were calculated and are compared with the measured results. The results from the table showed that the elemental compositions of the stearic acid and the separated solid were very similar and were close to the theoretical prediction for pure stearic acid. The nitrogen level was near zero in the separated solid. These results prove that the separated solid was stearic acid rather than the acid soap, which in contrast would have contained a significant amount of nitrogen.

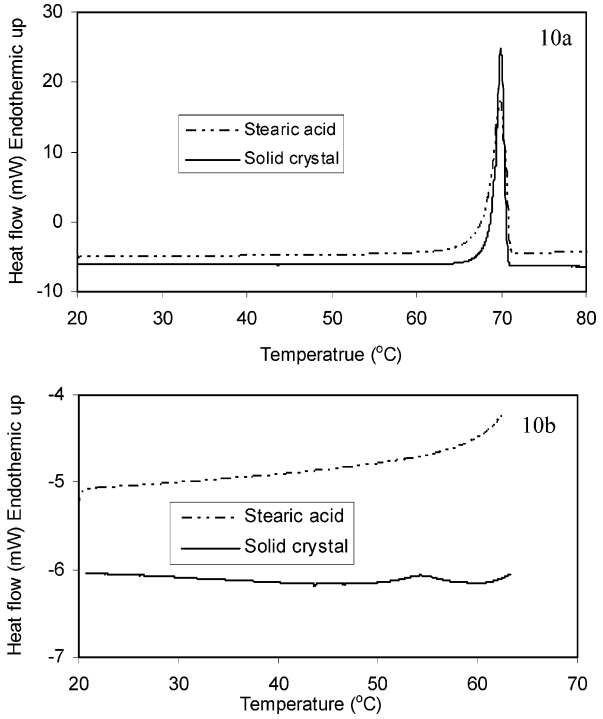


Figure 10. DSC heating curves of the separated solid and stearic acid received from Fisher Scientific: (a) the whole heating curves and (b) the magnified part of the heating curves. Scanning rate = 1 deg/min.

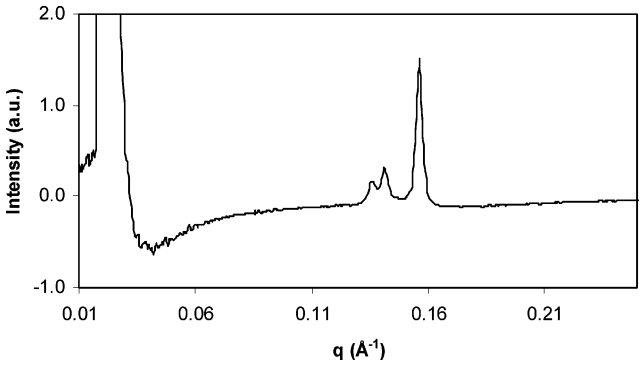


Figure 11. SAXS profile of the separated solid at room temperature.

3.3.2. DSC Analysis. The thermal behavior of separated solid was measured with DSC in a heating−cooling−reheating circle at a scanning rate of 1 deg/min and the results of first heating are plotted in Figure 10. The first heating curve showed two melting peaks at ca. 54.3 and 69.9 °C, respectively (see Figure 10b). The peak at lower temperature was very broad and the enthalpy was 2.2 J/g while the higher temperature was very sharp with an enthalpy of 198.6 J/g. The cooling curve only showed one exothermic peak with an enthalpy of 196.1 J/g at 66.5 °C. The reheating curve also showed one endothermic peak at 70.3 °C, enthalpy 196.4 J/g. The DSC melting curve of C form stearic acid from the supplier (Figure 10 dashed line) showed only one melting peak at 69.8 °C, enthalpy 196.6 J/g.

3.3.3. X-ray Diffraction and IR Spectroscopy. SAXS diffraction of the separated solid is plotted in Figure 11. Three peaks appear. The bilayer lengths of the three peaks are 40, 44.7, and 46.6 Å, respectively.

The IR spectrum of the separated solid is plotted in Figure 12. The main band present in the diagnostic region is at 686 cm^{-1}, slightly shifted up from that of the unseparated sample, with reduced intensity at frequencies just below this.

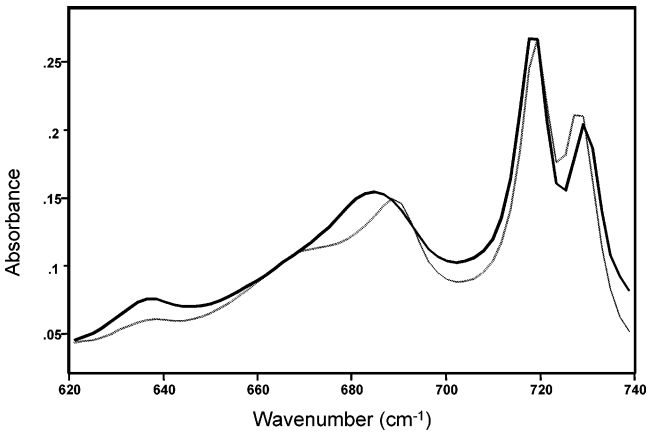


Figure 12. IR of the separated solid (solid line) and C form stearic acid (dashed line) at room temperature.

4. Discussion

4.1. Structural Analysis. *4.1.1 Heating and Mixing.* When the 80 °C TEA solution was added to the molten stearic acid a viscous, translucent, low birefringent gel was formed. The pH of the TEA solution was 9.3. The pH of the mixture was 7.2. The X-ray results showed a lamellar liquid crystal of long spacing of 174 Å. The change in pH indicates a neutralization reaction occurred between the TEA solution and the molten stearic acid. The lack of oil droplets in the micrographs indicates that there was no free stearic acid left. The ratio of unneutralized to neutralized stearic acid chains was 2:1. Previous study[10] showed a 2:1 TEA acid soap was present for the anhydrous system. Similar hydrated systems of partially neutralized alkali acid soaps show lamellar liquid crystal phases with similar pH values.[1,11,19−21] At 80 °C the sample was therefore a 2:1 acid soap lamellar liquid crystal phase.

4.1.2. Immediately on Cooling. Immediately on reaching room temperature, the unseparated sample was a more viscous translucent gel of low birefringence that was composed of multilamellar spheres. The pH was 7.5, slightly higher than the pH 7.2 at 80 °C. The SAXS results indicate only a swollen lamellar gel is present with a long spacing of 286 Å. The DSC results support this conclusion by showing a single peak on heating that corresponds to the transformation of the lamellar gel into a lamellar liquid crystal. Previous studies[1,11] on nonequilibrium alkali acid soap systems show that immediately on cooling an acid soap lamellar liquid crystal transforms into an acid soap lamellar gel.

4.1.3. 1 to 5 h. The samples translucence is gradually lost as the sample turns white. The birefringence increases and platelets start appearing together with the spheres. The SAXS shows the gel phase is reduced in long spacing and a peak has appeared at 40 Å indicating the presence of crystalline stearic acid. The DSC results show a small endothermic shoulder before the major gel to lamellar liquid crystal transitions.

4.1.4. 5 to 24 h. The sample now appears increasing pearly white. The birefringence has become very prominent and the microstructure is dominated by platelets rather than spheres. The SAXS results show a very broad peak at high q indicating a loss of the gel structure while the peak at 40 Å dominates indicating the presence of crystalline stearic acid. At 22 h the 40 Å stearic acid peak is abnormally broad to be a pure C form stearic acid. The DSC shows an increased peak area and a lowered onset temperature of the shoulder peak followed by the gel to lamellar liquid crystal transition.

4.1.5. 1 to 99 days. The sample separated into an opaque liquid phase and a pearly solid phase composed of large platelike crystals. The pH of the sample was 9.1, which was much higher than the initial pH of the cooled sample that was 7.5 but slightly lower than the pH of pure TEA solution at room temperature, which was 9.6. The SAXS showed three crystalline peaks in the range 40, 44.7, and 46.6 Å suggesting several polymorphs of stearic acid were present. The bilayer thicknesses for the A, B, C, and E forms of stearic acid are 46.5, 43.9, 39.8, and 44.2 Å, respectively.[4,11−18] The X-ray results indicate that three polymorphs, the C, the A, and either the E or B forms of stearic acid crystals exist in the aged sample. The long spacing of the E and B forms are very similar and therefore the SAXS is unable to resolve which form is present.

There are a number of publications that have used IR spectroscopy to identify the different polymorphs. A number of changes can be observed in the spectra for the different polymorphs. The most diagnostic have been detailed by Kobayashi et al.;[22−24] these are bands due to the in-plane deformation of the carbonyl, δ (C═O). Thus for the C form a doublet is observed for both the cis and trans form present.[25] The two bands are at 690 and 670 cm^{-1}. The B and E forms only have one band, as only the cis is present, but at different frequencies, 641 and 684 cm^{-1}, respectively. Kobayashi has not studied the A form, but spectra of it have been published in earlier work,[26,27] with a band observed at 677 cm^{-1} for δ (C═O).

The IR spectrum of the aged sample (99 days) was measured and shown after the subtraction of a water spectrum in Figure 9. It shows the main region of interest—the strongest band is observed at 685/6 cm^{-1} with some further intensity at lower frequency. This suggests the sample is in the E form with a contribution from C, which shifts the band position from that observed for E toward that of C. The lower frequency intensity could be from some polymorph A being present, but this is complicated by the fact that the second C band is also observed at a close frequency so a clear assignment is difficult, but nothing is observed for B.

DSC shows that a fixed enthalpy is reached for the shoulder peak prior to the gel to liquid crystal transition. This suggests the transformation has finished.

We therefore conclude that the stored sample is composed of the C, E, and A forms of stearic acid in a TEA solution, which must have some neutralized stearic acid in it because the pH was slightly lower than that for pure TEA solutions.

4.1.6. Separated Sample after 3 Months. When separated off, the aged solid component had an elemental analysis compatible to stearic acid rather than a 33% neutralized acid:soap. The SAXS suggested the C, A, and either the E or the B forms of stearic were present. The IR suggests that the main forms present are still E and C and with no clear evidence for the presence of the A form. As with the wet sample no B is observed. The DSC of the separated solid shows a very dominant peak at 69.9 °C of enthalpy 198 J/g; these values indicate the presence of the C form of stearic acid. The DSC also shows a broad and very low enthalpy peak at 54 °C. It was reported that A and E forms of stearic acid are not stable at high temperature and would undergo a phase transition to form the most stable C form.[15,16−18] The transition temperature of A to C form is 54 °C and E to C is 45 °C and they are not reversible. The enthalpies of these two transitions are 4.6 and 15.5 J/g. Therefore in the first heating, see Figure 10, the small low-temperature peak is due to a polymorph transition and the transition at 69.9 °C is the melting point of the C form. During cooling only the

C form is formed from the melt. Therefore the reheating behavior reflects the existence of the C form only.

4.2. Reactions and Physical Transformations during Storage. In summary, the two initial liquids, molten stearic acid and hot TEA solution, on mixing form a 2:1 acid soap lamellar liquid crystal. On cooling this transforms to a 2:1 acid soap lamellar gel phase. On storage this separates into stearic acid crystals which appear to be the C form, and a TEA solution that contains some neutralized stearic acid. On further storage C, E, and A form stearic acid crystals form. We now discuss the chemical and structural transformations that must have occurred during the process to result in this product.

Neutralization is a chemical reaction, also called a water forming reaction, in which an acid and a base or alkali (soluble base) react and produce a salt and water. In this system the reaction between TEA aqueous solution and stearic acid is represented by

$$HN(CH_2CH_2OH)_3OH + HA \text{ (stearic acid)} \leftrightarrow HN(CH_2CH_2OH)_3\,A + H_2O$$

Neutralization is always an exothermic reaction. The degree to which the neutralization is completed is determined by the system's reaction constant, which is a function of the temperature for a fixed component. Hydrolysis is the reverse of neutralization, so for this system,

$$HN(CH_2CH_2OH)_3\,A + H_2O \leftrightarrow HN(CH_2CH_2OH)_3OH + HA \text{ (stearic acid)}$$

Hydrolysis is always an endothermic reaction. To move the reaction to the left or right, either the temperature of the system must be altered or the relative concentrations of the components must change. Increasing the temperature favors increasing the endothermic reaction and therefore hydrolysis. Likewise decreasing the temperature will favor neutralization.

The results obtained from current experiment showed that the neutralization takes placed readily at 80 °C while significant hydrolysis reaction occurs on cooling. This is in apparent contradiction to the descriptions of neutralization and hydrolysis above; however, the changes of the reaction direction are due to the changes of the physical state of reaction reagents and products. In the neutralization reaction, stearic acid, one of the reagents, is a solid phase at ambient temperature. It changes to a liquid phase at 80 °C, which drives the neutralization reaction with adequate mixing. The product TEA stearate forms a homogeneous phase with the remaining fatty acid in water creating the liquid lamellar crystal, which also drives neutralization at this temperature. At room temperature the reaction moves toward hydrolysis since the product, stearic acid, solidifies and separates from the aqueous solution. Since the lamellar gel phase is a metastable phase and will crystallize into a three-dimensional ordered structure it would be expected that the crystalline bilayer is more stable if a small counterion, such as H^+, exists between the bilayer head groups rather than the large counterion of TEA. The consequence of this effect is to replace the TEA counterions between the crystalline bilayer with H^+. For the doubly weak salt, NH_4CN, it was reported that a 47% degree of hydrolysis was observed for a 0.1 M solution.[28] TEA is a weak base and stearic acid is a weak acid that is also insoluble in water. It is thus expected the hydrolysis reaction would occur more pronouncedly for the TEA and stearic acid in water at room temperature than the NH_4CN salt. Hydrolysis of alkaline soaps such as potassium stearate was studied before.[29−30] Stearic acid crystal was formed at the soap concentration below 10^{-3} M. No hydrolysis above the concentration was discovered. At the concentration of around 0.5 M studied in the current work the acid soap crystal and soap crystal of potassium stearate were formed due to the hydrolysis instead of stearic acid crystals. This is because the alkaline base is a strong base while TEA is a weak one.

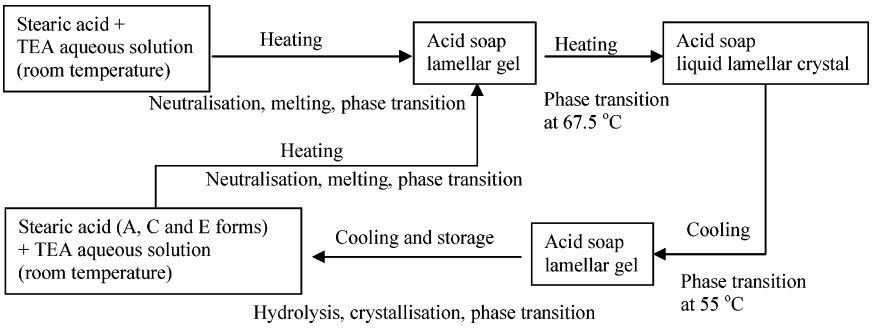
The DSC heating curves of the aged samples showed an endothermic shoulder peak at a lower temperature, onset point at ca. 30 °C, than that of the gel to lamellar liquid crystal transition or the stearic acid melting temperature. This endothermic peak results from a complex process that involves the neutralization between stearic acid and the TEA solution and the formation of the lamellar gel phase of the 2:1 acid soap. The hydrocarbon chains of the gel phase are arranged hexagonally packed with one-dimensional freedom, a change from the close packing crystal of stearic acid.[11] This change is significantly endothermic. During the storage the opposite process occurs. The hydrolysis reaction translates TEA stearate back to stearic acid and the hexagonal packing hydrocarbon chains of the gel phase crystallize into the close packed crystal of stearic acid, a transition that is exothermic. Since the hydrolysis reaction occurred slowly after cooling the heating curve of the aged sample depends on the storage time and more directly on the degree of completion of the hydrolysis reaction. In the current system the hydrolysis reaction seems to finish in ca. 24 h as shown by microscopy, DSC, and X-ray results.

When stearic acid was mixed with the TEA solution at 80 °C its pH value decreased to 7.2 as the neutralization reaction occurred. The decrease of pH value is due to the partial neutralization (33%) of the stearic acid with TEA. Cistola et al. reported a comprehensive study on pH variation of fatty acid and potassium soap at different neutralizations. It was found that a pH plateau of ca. 7.3 was obtained when an acid soap was formed at neutralizations below the formation of a free soap.[4,19] The increase of pH during the storage time suggests that the hydrolysis reaction taking place created free TEA molecules in aqueous solution. The final pH value of 9.1, which is slightly lower than that of pure aqueous TEA solution of pH 9.6 at room temperature, suggests that there is still some neutralized stearic acid in the system as the hydrolysis reaction is not finished completely for a weak acid and weak base.

Four different crystalline formats were identified for stearic acid, namely the A, B, C, and E forms. The C form is the most stable one and melts at 69 °C.[16,17] Pure C form is formed via crystallization from the melted stearic acid and also from solvent recrystallization. Polymorphism usually occurs when stearic acid recrystallizes from organic solvents. The properties, for example the polarity, of the organic solvents and the cooling rate of the recrystallization process can influence the polymorph formed.[13−16] For example, B and C forms have been obtained from benzene and C, B, and A forms from acetone. In the current study polymorphs of A, E, and C forms were obtained from the partially neutralized stearic acid in water. It is thus believed that the polymorphism observed results from the crystallization of nonneutralized stearic acid (possible for the C form) and from stearic acid produced by the hydrolysis reaction (possible for A and E forms). A more detailed mechanism study is needed. The strong pearlesence appearance of the separated crystals may also result from the polymorphism of the stearic acid.

Scheme 1 illustrates the complex chemical and physical changes of stearic acid and aqueous TEA solution at different temperatures.

SCHEME 1



4.3. Unidentified Zone of TEA Stearate Aqueous Phase Reported by Warnheim et al. Aqueous phase behavior of fully neutralized fatty acids with TEA has been reported by Warnheim[7,8] and Friberg.[9] Crystalline lauric acid was identified from TEA laurate aqueous solution at low surfactant concentration, up to 7%.[8] For stearic acid a large undetermined zone or miscibility gap in the phase diagram, up to 30% surfactant concentration, at room temperature was reported.[7] It was claimed that this is due to the existence of a small amount of free stearic acid and TEA, ca. 2% due to the incomplete neutralization in the system. The experimental results from current work suggest that this unidentified zone or miscibility gap is mainly caused by the hydrolysis of TEA stearate, which produced significant amounts of stearic acid crystals and TEA aqueous solution. It is further possible that the miscibility gap could extend to higher TEA stearate concentrations with prolonged storage time as the higher concentration of TEA stearate may slow down dramatically the hydrolysis reaction speed due to the high viscosity.

4.4. Multilamellar Spheres. Multilayer lamellar vesicles have been observed before for the dilute systems of ionized short chain fatty acids or unsaturated fatty acids, for example, oleic acid systems neutralized with an alkaline base at temperatures above the hydrocarbon chain's melting point.[31−32] These vesicles were made by methods such as titration and surface absorption. Hargreaves and Deamer[32] prepared large vesicles from saturated C8−C16 chain fatty acids. Dilute sodium or potassium salts of the fatty acids were dissolved in water and hydrogen chloride was used to partially neutralize the fatty acid salts at temperatures above the fatty acid melting point. Their results showed that large vesicles exist above the melting point, i.e., in the liquid crystalline phase. Below the melting point flat and angular crystals were formed. The crystals were found to be acid soap crystals. In the current work the multilamellar spheres observed immediately after cooling were formed by the stearic acid partially neutralized with TEA. These spheres were observed at temperatures well below the hydrocarbon chain melting point. The spheres were not stable but formed stearic acid crystals with a platelet structure during storage. It was observed by the current authors (see the pictures in the Supporting Information) that the multilamellar spheres from partially neutralized long chain fatty acids using TEA can be stabilized at room temperature for long times if mixed chain length fatty acids, for example, palmitic acid and stearic acid, were used. This effect was also seen if long chain fatty alcohols, for example, cetyl alcohol, were added to the bilayer structure.

5. Conclusion

This paper describes the interaction between partially neutralized stearic acid with TEA and water at the high surfactant concentration of 20%. The experimental results show that a neutralization reaction takes place between stearic acid and TEA at 80 °C. The partially neutralized stearic acid, the unneutralized stearic acid, and water form a liquid lamellar phase. On cooling the liquid lamellar phase changed to a lamellar gel phase and formed spherical balls with a diameter of a few microns. The gel phase then goes through a hydrolysis reaction and creates plate-like stearic acid crystals of polymorphs A, E, and C. In the described experimental conditions the hydrolysis finished in approximately 24 h. The resultant stearic acid crystals gave rise to a strong pearlescent appearance.

The neutralization and hydrolysis reactions at different temperature observed in the current system result from the fact that both TEA and stearic acid are weak base and acid, respectively, and the complex changes of the physical state and the phase behavior of the reagents and products at different temperatures.

The results obtained from this work illustrate the dramatic difference of TEA based acid soap in comparison with alkaline based acid soap in terms of the interaction with water at room temperature. They add new insight to our understanding of the structure and behavior of long chain fatty acid and their acid soap complexes. The significant hydrolysis reaction at room temperature also gives rise to applications of TEA acid soap in terms of controlling the wash property of soap bars containing of TEA acid soap.

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Supporting Information Available: Cryo-sem images of multilayer lamellar vesicles made from a mixture of stearic acid (50% by weight) and palmitc acid (50% by weight) with a neutralization degree of 33% with TEA and a total surfactant concentration of 20% by weight. This material is available free of charge via the Internet at http://pubs.acs.org.

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