Acid Soap and Phase Behavior of Stearic Acid and Triethanolamine Stearate

S. Zhu,* M. Heppenstall-Butler, M. F. Butler, P. D. A. Pudney, D. Ferdinando, and K. J. Mutch

Corporate Research, Unilever R & D, Colworth Lab, Bedford, MK44 1LQ, UK

Crystals of partially neutralized stearic acid with triethanolamine (TEA) were prepared by mixing these two materials above 80 °C and then cooling. The crystalline composition and the structure and melting behavior of the resultant products were characterized with small-angle and wide-angle X-ray diffraction, thermal analysis, microscopy, and infrared spectroscopy. It was discovered that an acid−soap complex of 2:1 fixed stoichiometric ratio exists between stearic acid and TEA stearate. A binary phase diagram of stearic acid and TEA soap is built based on the experimental results; this is the first published record of a binary phase diagram for amine-based soap. Its behavior is significantly different from that of binary systems of fatty acid and alkali soap.

1. Introduction

Acid soap and the phase behavior of alkali long-chain fatty acids have been studied extensively for more than 100 years for both academic and industrial interests.[1−4] Acid soap was found to be a fixed stoichiometric ratio complex formed between the acid and the alkali soap due to the strong interaction, hydrogen bonding, of the headgroups.[1−7] The acid soap composition, crystalline structure, and binary phase diagrams of potassium or sodium soap have been published widely for fatty acids with different chain lengths and saturated or unsaturated hydrocarbon chains.[1−7] There are still questions remaining, however, regarding the details of the headgroup interactions and what determines the fixed stoichiometric ratio between the acid and the soap and how the size of the counterions, potassium versus sodium, contribute to the complex crystalline structure and the stoichiometric ratio. For example, potassium soap is reported to form mainly 1:1 ratio acid soap, whereas sodium soap can form a range of ratios of 3:2, 2:1, 1:1, 2:3, and so forth.[4,6]

In contrast to the rich literatures about alkali soap and acid soap, there have been only a few publications on the phase behavior of amine soap in water,[8−10] and no work on dry amine soap and acid soap has been published in the open literature. However, alkanolamines, such as triethanolamine (TEA), are used widely in cosmetic products to replace potassium hydroxide or sodium hydroxide to neutralize fatty acids and create an anionic surfactant with a quartenary ammonium counterion.[11] It is therefore highly important to understand amine soap properties and identify if an acid−soap complex or a plurality of complexes exist between the acid and the amine soap. This is thus our main motivation for carrying out the current study. This work not only provides useful knowledge for the optimization of cosmetic formulation and control of the crystalline composition in the final product but also increases our understanding of acid soap and headgroup interactions for a system neutralized with a weak base and with a very large counterion size.

2. Experimental Method

2.1. Materials and Sample Preparations. Stearic acid and triethanolamine (TEA) were provided by Fisher Scientific. The quoted purity of stearic acid and TEA being 98 and 99%, respectively. The neutralization degree of stearic acid is calculated based upon the molar ratio of stearic acid to TEA, and samples with neutralization degrees of 5, 13, 20, 25, 33, 40, 50, 60, 70, 80, 85, 90, and 100% were prepared.

2.2. Preparation of Stearic Acid and TEA Stearate Mixtures. Stearic acid was melted at 80 °C in a water bath. TEA was then added slowly to the melt at 80 °C while being stirred. The temperature of the mix was then increased up to 95 °C to obtain an isotropic solution. The solution was then cooled and solidified in an ambient environment. The resulting solid was ground down to form a powder. The powder was stored in a closed container for at least 7 days before it was analyzed. This preparation method has been used previously to prepare alkali acid soap crystals.[1,5]

2.3. Thermal Analysis. Five to 30 milligrams of sample were placed inside a sealed stainless steel pan. A differential scanning calorimeter, Perkin-Elmer DSC7, was used to analyze samples at a scanning rate of 1 °C/min. A different DSC (Diamond from Perkin-Elmer) was used to scan the samples at 0.1 °C. The temperature range scanned was 10−120 °C.

2.4. Optical Microscopy. The powder sample was placed between two optical glass slides and placed on a temperature-controlled microscope stage (Linkam UK), so the sample temperature could be controlled under the microscope. The sample was then observed using transmitted brightfield and polarized light at a scanning rate of 1 °C/min.

2.5. Time-Resolved SAXS/WAXS/DSC. 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 set up have been described elsewhere.[12] The high-intensity, low-divergence beam monochromatic had a wavelength approximately that of Cu Kα radiation ($\lambda = 1.54$Å). The scattering vector to channel number calibration for the SAXS detector was performed using wet rat tail collagen. The 2θ channel numbers of the wide angle detector were calibrated using high-density polyethylene.

The sample holder was a DSC pan (TA instruments) with a 3.5-mm-diameter mica window. The window was made of high

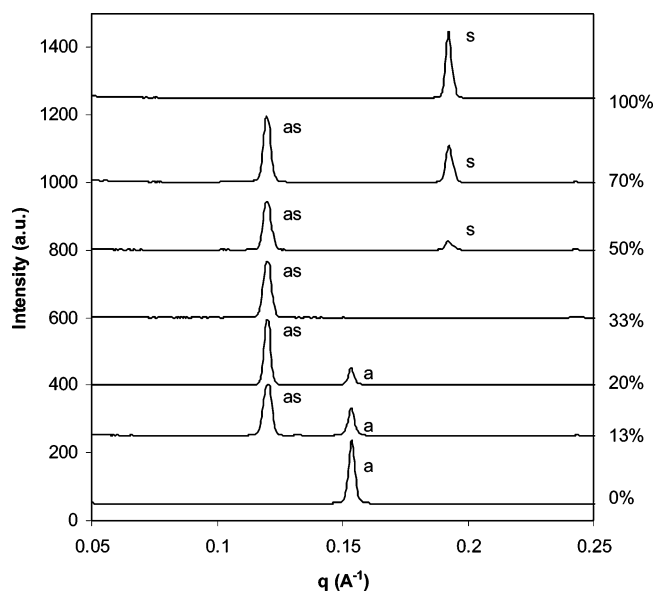* Corresponding author. E-mail: shiping.zhu@unilever.com

Figure 1. SAXS diffraction peaks (first order) of stearic acid at different neutralizations at room temperature. a: acid; as: acid soap; and s: soap.

Figure 2. WAXS diffraction peaks of stearic acid at different neutralizations at room temperature. a: acid; as: acid soap; and s: soap.

quality, pure, scratch free, and nongreasy mica (Attwater Group) and was 25 μm thick. Holes (3.5 mm) were punched in the aluminum pans and 5-mm disks of the mica were glued in place using epoxy. The DSC sample pans, each holding about 60 mg of sample, were placed in a Linkam hot stage connected to DSC software that was used to give an automated liquid nitrogen cooled known temperature program that was synchronized with the X-ray data acquisition software so that X-ray data collection was initiated at the start of heating.

A SAXS/WAXS static (exposure time 60s) was taken for all of the samples. A heating rate of 10 °C/min was applied from 20 to 105 °C for the 100% neutralized sample and 20 to 95 °C for the rest of the samples. Data were collected every 10 s, that is, every 1.67 °C.

2.6. Infrared Spectroscopy (IR). The experiments were carried out using a biorad FTS 6000 FTIR spectrometer. The samples were measured using a diamond ATR "golden gate" with a heatable top plate with a quoted temperature accuracy of 1 °C (Geasby Specac U.K. Ltd). Spectra were taken at 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.

3. Results and Discussion

A neutralization reaction takes place readily when stearic acid and TEA are mixed together at a temperature above the melting point of stearic acid. The product being the salt TEA stearate, otherwise known as TEA soap. It is well known that acid−soap complexes are formed between alkali soap and stearic acid, which is a new crystalline phase and is different from the respective alkali soap and stearic acid. Therefore, our first experimental work is to identify whether the resulting TEA soap forms an acid−soap complex with stearic acid using X-ray diffraction and IR.

3.1. Static X-ray Diffraction at Room Temperature. SAXS and WAXS of stearic acid neutralized to different degrees were obtained at room temperature. Figures 1 and 2 show the SAXS
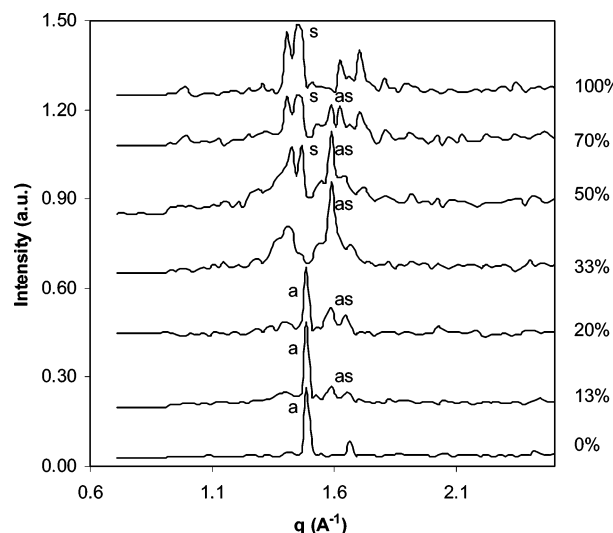
and WAXS diffraction peaks, respectively, for neutralizations of 0, 13, 20, 33, 50, 70, and 100% mixtures. The SAXS curves show that stearic acid possesses a bilayer crystalline structure with a repeat distance of 40.8 Å. This repeat distance is very close to the value reported for stearic acid.[1,13] At 13% neutralization, a new bilayer crystalline structure with a repeat distance of 52.2 Å appears in the diffraction curve in addition to the one from the crystalline stearic acid. At 20% neutralization, the diffraction pattern is the same as the 13% sample but the intensity ratio of the new peak to the acid peak has increased. This result indicates that the new crystalline phase volume increases, whereas the acid crystalline phase volume decreases with increasing neutralization. At 33% neutralization, only one bilayer structure with a repeat distance of 52.2 Å is observed. With further increases in neutralization to 50% and 70%, another peak appears corresponding to a repeat distance of 32.6 Å in addition to the peak at 52.2 Å. The intensity of the 32.6 Å peak increases with increasing neutralization. At 100% neutralization, only one peak at 32.6 Å is observed.

Previous phase studies on stearic acid and its alkali soap reported that fixed stoichiometric ratio complexes of acid soap were formed when stearic acid was partially neutralized with sodium or potassium hydroxide.[1−8] For example, a 1:1 acid soap between fatty acid and potassium soap was reported for fatty acids for a range of different chain lengths, for example, from C12 to C18. For sodium soap, the fixed stoichiometric ratio varied from 3:2 to 1:1, and to 5:2 with the increase of the neutralization degree.

The SAXS results suggest for the first time that an acid/ stearate TEA acid soap exists. The crystalline phases found are the following: stearic acid (40.8 Å), TEA stearate (32.6 Å), and a 33% neutralized compound with a repeat distance of 52.2 Å, which corresponds to the acid to soap ratio of 2:1.

The repeat distance measured in this work for stearic acid crystals using SAXS is 40.8 Å, indicating that the acid chain is not perpendicular to the planer axis. The repeat bilayer length of the stearic acid is very close to the values of C-form of stearic acid crystals.[1,13] The repeat bilayer distance, 52.2 Å, of the TEA acid−soap complex is slightly longer than that of alkali acid soap reported by literature. A repeat bilayer distance of 50.4 Å was reported for potassium acid soap with the hydrocarbon chain perpendicular to the planer axis.[1,5] Cistola et al.[14] reported that 1:1 potassium acid soap of stearic acid has a bilayer length of 51.2 Å. The 3D size of the TEA counterion is calculated to be

Stearic Acid and Triethanolamine Stearate

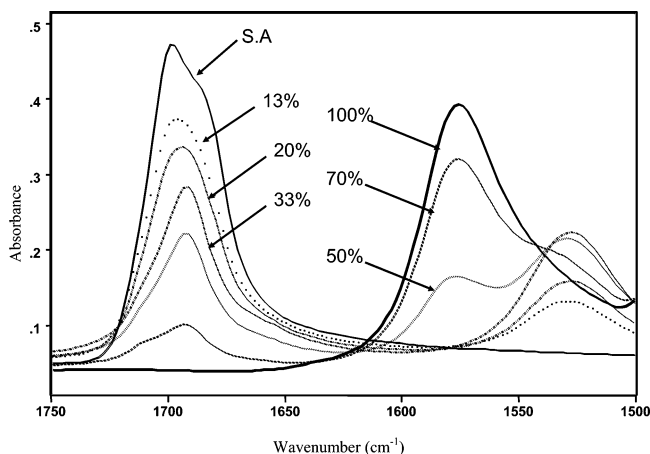*J. Phys. Chem. B, Vol. 109, No. 23, 2005* **11755**

Figure 3. IR spectra of the carbonyl/carboxylate region of stearic acid at neutralizations of 0, 13, 20, 33, 50, 70, and 100% at room temperature.

2.2, 7.7, and 7.7 Å according to the bond lengths and angles of TEA ions. It is possible that the hydrocarbon chain of the TEA acid soap is also perpendicular to the planer axis if the TEA counterion fits between the headgroups of the bilayer with its shorter dimension. Further X-ray study is required to prove this.

The most striking difference is observed from the repeat distance of TEA stearate compared with other soaps with a similar chain length. Potassium stearate was reported to have a tilted bilayer structure with a repeat distance of 42 Å and a tilted angle of 55.8°.[1] A recent study of the crystalline structure of ammonium stearate showed that a long spacing of 73.9 Å exists with 4 hydrocarbon chains arranged in a zigzag pattern.[15] The repeat distance of TEA stearate measured by this work is 32.6 Å. There are two possibilities that could account for such a short long spacing. One is that the hydrocarbon chain adopts a bilayer structure with a very small tilted angle, ca. 38°. The other is that the TEA soap adopts an interdigitated single-layer structure where the long spacing measured by X-ray would be close to a single chain length of TEA stearate. X-ray and molecular simulation on this crystal structure are currently being carried out. The result will be reported soon.

The WAXS diffraction profiles showed multiple diffraction peaks reflecting the complex ordered structuring between the hydrocarbon chains. However, it is possible to differentiate the three crystalline structures from the peaks. For example the peak with $q = 1.485$ (A^{-1}), $d = 4.23$ Å, is seen only for the samples with the neutralization degree below 33%, indicating that it is from the stearic acid crystal. For the acid soap crystal, the peak, at $q = 1.585$ (A^{-1}), $d = 3.96$ Å, is seen when acid soap crystal is present. The peak, at $q = 1.465$ (A^{-1}), $d = 4.29$ Å, is seen when free soap is present above 33% neutralization.

3.2. Infrared Spectroscopy at Room Temperature with Changing Neutralization. Infrared spectroscopy has been used to study a number of fatty acids and alkali soaps, and the spectra are generally well understood (ref 16 and refs therein). There has also been some work on alkali acid−soap complexes.[3,6,13,17] However there has been no FTIR work on TEA acid soaps. When stearic acid is neutralized, the biggest changes are observed in the region between 1500 and 1750 cm^{-1}, which encompasses the C=O and COO^{-} stretches, see Figure 3.

It can be seen that stearic acid shows only a carbonyl peak, positioned at 1698 cm^{-1}, and shows no COO^{-} peak. This is expected because most fatty acids exist in dimeric form, hydrogen bonded to another fatty acid molecule and hence have no dissociated COOH groups.[18,19] As soon as TEA is added to

neutralize the acid, a COO^{-} band emerges at approximately 1530 cm^{-1}. The progression thereon is that the carbonyl band decreases in intensity and shifts to a slightly lower frequency, whereas the carboxylate peak increases in intensity and also shifts to a slightly lower frequency. This ties in with the observation with alkali acid soaps by Lynch et al.[3] that suggested that acid−soap crystals maintain some carboxylic-acid-like character and some carboxylate-anion-like character. Above 33% neutralization, a new feature is observed in the spectrum at approximately 1580 cm^{-1}; this band is assigned to soap.[3,6] As the neutralization is increased further, this soap carboxylate band increases and the acid−soap band decrease; the carbonyl peak continues to decrease as before in both intensity and frequency. Thus, there is no longer acid soap being formed but instead the further addition of TEA producing soap, giving an acid−soap, soap mixture rather than the acid−soap, acid mixture that is observed below 33% TEA. These bands can be used to give the degree of neutralization present for each sample and its make up of acid, soap, and acid−soap. This is reported in detail elsewhere.[16]

Information is also available on the alkyl chain packing from various carbon−hydrogen modes. These are discussed with relation to heating effects in section 3.5. The full assignment and interpretation of the whole spectrum are discussed more fully elsewhere.[16]

3.3. Dynamic X-ray Results as a Function of Temperature. To investigate the structural information between the phase transitions, we irradiated the crystals with various degrees of neutralization with X-rays while heating at 10 °C/min. The X-ray scattering data were collected and averaged every 10 s. Both SAXS and WAXS were recorded. Figures 4−7 show the SAXS and WAXS data with the increase of the temperature for 20%, 33%, 70%, and 100% neutralized samples.

Table 1 summaries the structural changes of the samples as the temperature increases, measured by X-ray diffraction. For the non-neutralized stearic acid, X-ray data only show a solid to liquid transition. At neutralizations between 0 and 33%, stearic acid and the acid soap coexist at room temperature. On heating, both crystals disappear at approximately same temperature and an isotropic liquid forms at higher temperatures. The 33% neutralized sample shows rather simple melting process on heating. It melts at approximately the same temperature as the acid and forms an isotropic liquid after melting. It is observed that during the melting process a broad and low intensity peak at 33 Å appears temporarily. It disappears once the acid soap crystal melts completely.

For neutralizations between 33 and 100%, for example, 70%, the melting process is more complicated than that at lower neutralizations. At room temperature, the acid soap and the soap coexist. With increasing temperature, the acid soap starts melting followed by the soap. During the melting process, a new peak at around 36 Å appears and its intensity increases significantly with further increase in temperature. With increasing temperature, the repeat distance decreases slightly. The peak disappears at around 90 °C. The diffraction peaks from WAXS disappear after the melting of the acid soap and the soap, indicating that the peak at 36 Å represents a lamellar liquid crystal phase.

The 100% neutralized sample shows one peak at 32.6 Å in the SAXS data. The soap melts when the temperature increases. A new peak at 36 Å appears while the soap is melting. The new peak intensity increases sharply after the soap peak disappears and then decreases with further increase in temperature. It disappears completely above 90 °C. The WAXS peaks

TABLE 1: Crystal Structural Changes with Increasing Temperature for Stearic Acid at Different Neutralizations[a]

neutralization temperature	0%	20%	33%	70%	100%
High	isotropic liquid	isotropic liquid	isotropic liquid	isotropic liquid	isotropic liquid
				lamellar liquid crystal	lamellar liquid crystal
↑				soap(s) + acid soap(s) + lamellar liquid crystal	soap(s) + lamellar liquid crystal
Low	acid(s)	acid(s) + acid soap(s)	acid soap(s)	acid soap(s) + soap(s)	soap(s)

[a] The acid, acid soap, and soap solid phases were all lamellar.
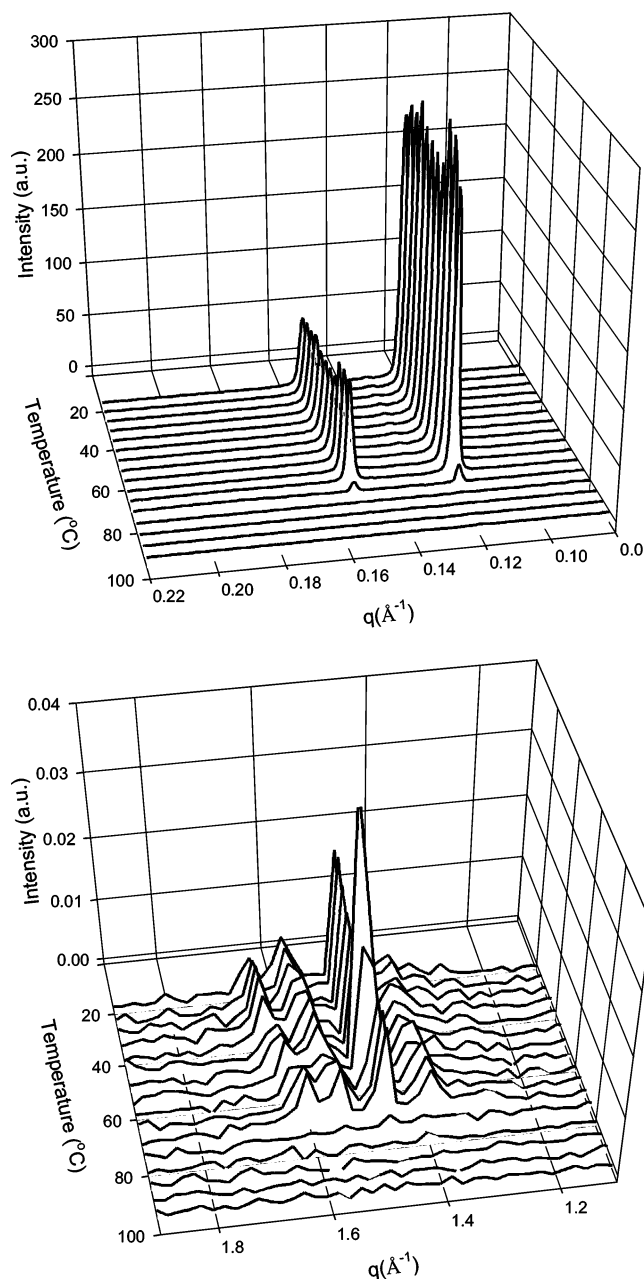
Figure 4. SAXS (top) and WAXS (bottom) of 20% neutralized stearic acid as a function of temperature.

disappear when the soap is completely melted, indicating the existence of a liquid lamellar crystal phase after the melting of the soap.

The observed overlapping of the liquid crystalline phase with the solid crystal phases for samples with a neutralization above 33% is due to the nonequilibrium effect of the X-ray method. At a 10 °C/min scanning rate, the onset and end temperatures of the crystal melting can span more than 10 °C because of the
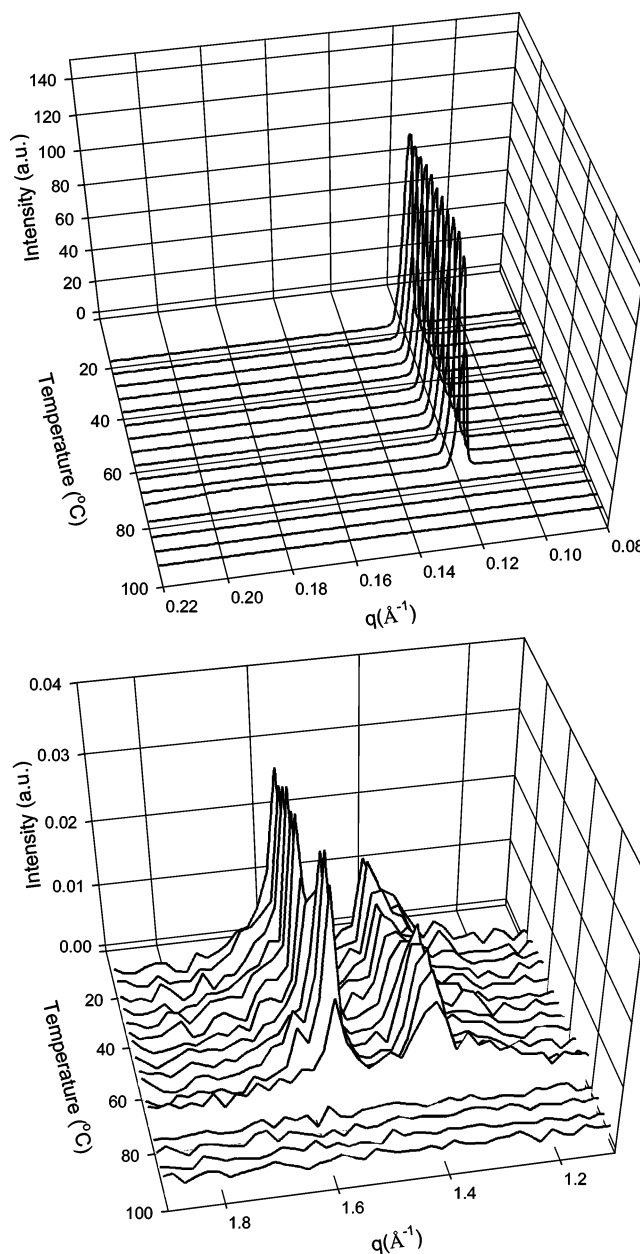
Figure 5. SAXS (top) and WAXS (bottom) of 33% neutralized stearic acid as a function of temperature.

impurity of the samples and crystals. The wide temperature ranges of the phase transitions were also observed in the DSC and microscopy methods.

3.4. DSC Thermal Analysis. The DSC heating curves of the samples at various neutralizations, obtained at 1 °C/min, are plotted in Figure 8. Stearic acid displays a melting peak at 69.3 °C. At 5% neutralization, another peak at 64.2 °C appears in addition to the acid peak that shifts in temperature to 68.5
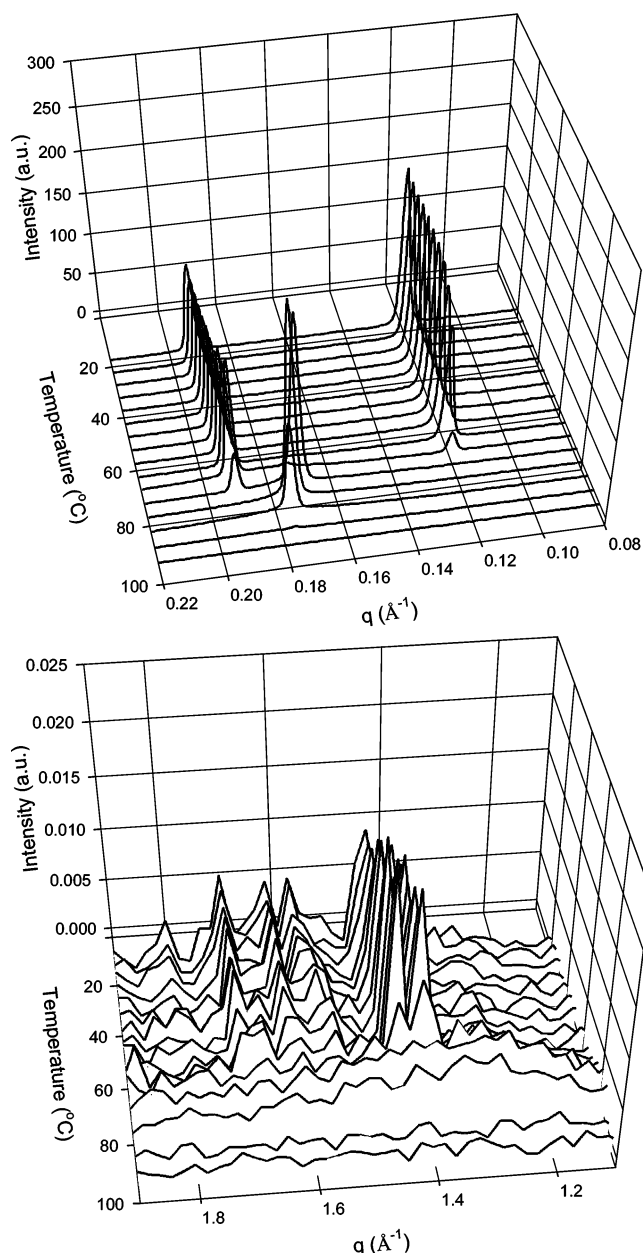
Stearic Acid and Triethanolamine Stearate

J. Phys. Chem. B, Vol. 109, No. 23, 2005 **11757**

Figure 6. SAXS (top) and WAXS (bottom) of 70% neutralized stearic acid as a function of temperature.

Figure 7. SAXS (top) and WAXS (bottom) of 100% neutralized stearic acid as a function of temperature.

°C. At 25% neutralization, a single melting peak is observed at 65.9 °C. At 33% neutralization, the composition for pure 2:1 acid−soap complex, a single melting peak at 67.9 °C is observed. DSC data suggest that there is a eutectic melting point around 25% neutralization between stearic acid and the acid soap crystals. The data also show that the acid soap has a slightly lower melting temperature than stearic acid.

The melting curves for the 70% neutralized sample show three transition temperatures. The first two are major transitions at 65.7 and 71.2 °C, corresponding to the melting peaks of the acid soap and the soap, respectively. The third is in the vicinity of 83 °C and has a very small transition enthalpy. It is also noticed that the transition at 83 °C, the liquid crystal melting transition, is complicated and involves two small peaks. A similar melting pattern is seen for the 85% neutralized sample, but the transition temperature of the acid soap is slightly lower, at 63.5 °C, the soap melting peak remains unchanged. The liquid crystal transition temperature increases to 87.9 °C. Again, the melting of the liquid crystal shows two melting peaks. At 100%
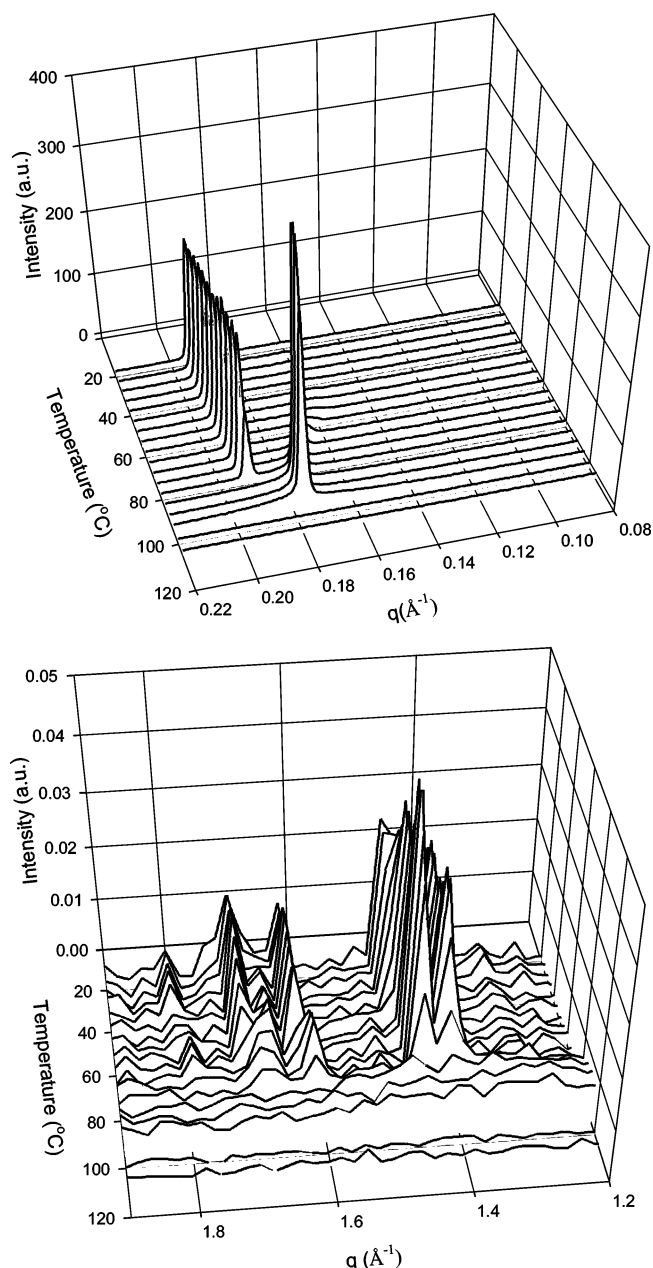
neutralization, the soap composition, a major transition is observed at 71.7 °C followed by small phase transition peaks at ca. 93 °C with a melting enthalpy of 0.87 kJ/mol. It is noticed that the liquid crystal melting transition, at 93 °C, shows multiple and complicated melting peaks including two melting peaks and negative enthalpy. The phase changes of the liquid crystalline phase were also observed under polarized light microscopy, see section 3.6. The temperature range of the transitions agrees well with the DSC data. The small enthalpy, ∼0.5 to 1 kJ/mol, of the liquid crystal phase transitions of potassium soaps was reported by Ishioka[20] at the appropriate high temperature for alkaline soaps, above 200 °C.

The melting enthalpies of stearic acid, acid soap, and soap are listed in Table 2. Stearic acid and acid soap require about the same amount of energy to melt the hydrocarbon chains, whereas the enthalpy for melting soap is about 20% higher than that of the other two crystals. For the alkali soap systems, the molecular interactions between the acid soap and soap molecules
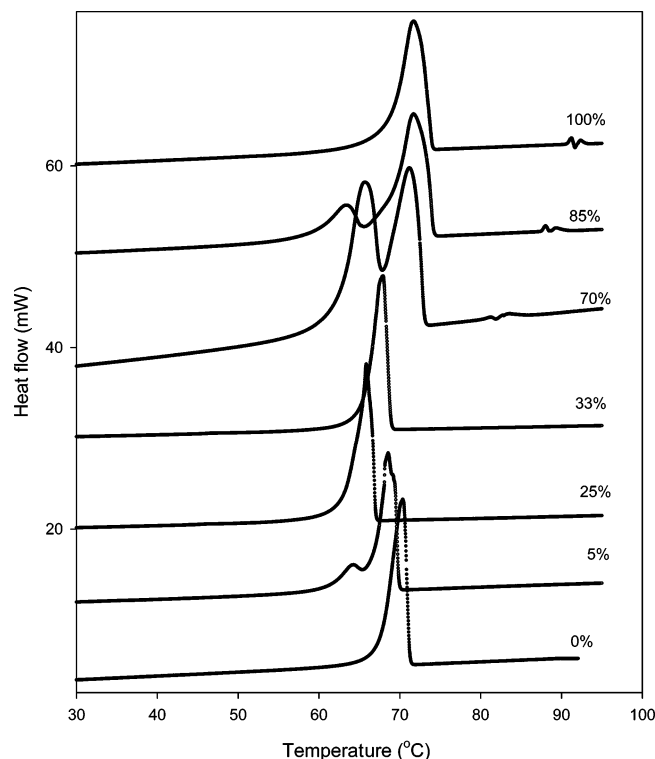
Figure 8. DSC heating curves of stearic acid at different neutralizations at 1 °C/min scanning rate.

TABLE 2: Phase Transition Temperature and Enthalpy of Stearic Acid, Acid Soap, and TEA Soap Crystals[a]

neutralization (%)	melting temperature (°C)	enthalpy (kJ/mol)	enthalpy (kJ/mol/chain)*
0	69.3	59.4	59.4
33	67.9	179.8	60.0
100	71.7	71.5	71.5

[a] Enthalpy (J/mol/chain) is calculated based on the number of the hydrocarbon chain in the crystal molecules. For example, one molar 2:1 acid soap consists of 3 molars of the hydrocarbon chain, whereas stearic acid and TEA soap have 1 molar of hydrocarbon chain per molar molecule.

were reported to be much higher than those for the corresponding acid molecules.[3,20]

To investigate further details of the phase transitions, we used a more sensitive DSC (Diamond) to scan the samples at 0.1 °C/min. The heating curves are plotted in Figure 9. The phase transitions and transition temperatures for the samples below 33% neutralization are very similar to those results obtained at 1 °C/min and therefore are not shown in the figure.

At high neutralization, above 70%, a small peak appeared between the main melting peaks of the acid soap and soap. The peak temperature is about 68 °C, and its intensity decreases with increasing neutralization. The peak temperature also decreases slightly with increasing neutralization. This small peak is not seen in the DSC results at 1 °C/min scanning rate.

Above the soap-melting temperature, small phase transition peaks appear because of the melting of the lamellar liquid crystal, see Figure 10 for enlarged details. The transition shows multiple peaks over a wide transition temperature range. The peak temperature increases with increasing neutralization, and the transition temperature range also varies with neutralization. For 40% and 50% neutralized samples, this transition is not observed in the DSC curves.

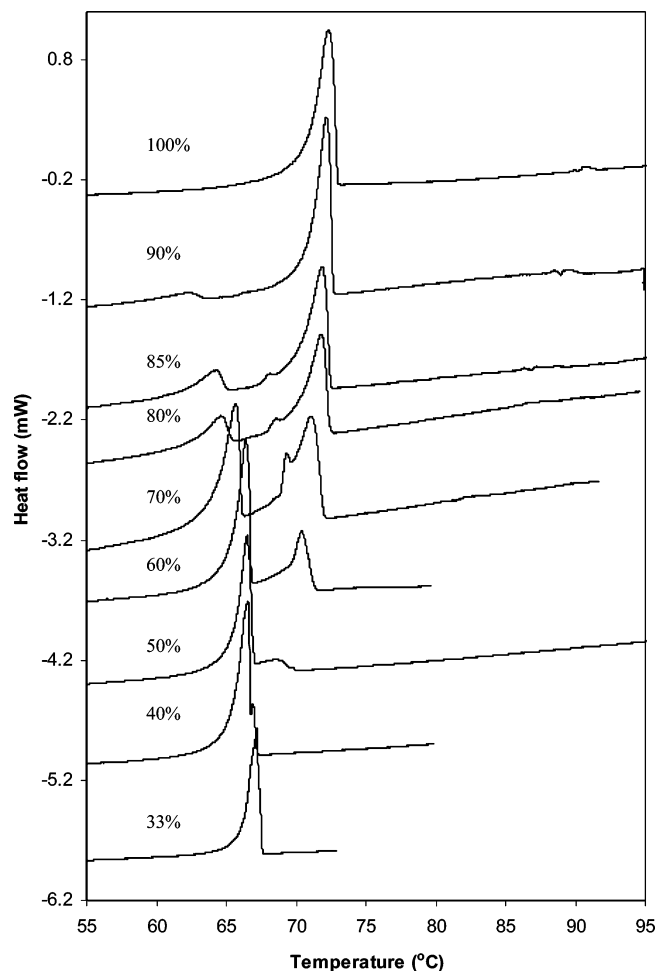X-ray results agreed well with the dynamic DSC results in terms of the main phase transitions on heating.

Figure 9. DSC heating curves of stearic acid at different neutralizations at 0.1 °C/min scanning rate.

3.5. FTIR Studies as a Function of Temperature. Spectra were collected for all of the samples as they heated to above the temperature for transition to isotropic liquid as determined by DSC. The spectra show a number of changes during heating. For reasons of brevity, a complete description of these changes and a full explanation of the interpretation is given elsewhere,[16] so only the salient points will be described here. By examining the behavior of difference vibrational modes originating from different parts of the molecules, one can plot and understand the complete phase diagram. The modes for this study are grouped into two, those relating to the alkyl chains and those relating to the headgroups.

3.5.1. FTIR of Alkyl Chains. The behavior of alkyl chains upon heating has been well studied by infrared spectroscopy. This understanding is based on the work of Snyder on alkanes.[21] Similar effects have also been observed in carboxylic acids and alkali soaps.[17] The effect of chain melting and so forth can be seen in a number of modes, but here we concentrate on two that show the transitions particularly clearly. The degree of disorder in an alkyl chain is known to be reflected in the νCH bands.[17] The symmetric CH_2 stretch frequency has been shown to shift in lipids with increasing disorder (ref 22 and refs therein). This mode is observed at approximately 2850 cm^{-1} and its frequency has been plotted against temperature for all of the samples. An example for 85% neutralization is shown in Figure 11. This shows three transitions, two around 60 to 70 °C and a smaller transition at higher temperatures. The first two appear to correspond to the acid soap and soap alkyl chains melting; the first smaller transition at 64 °C is due to the acid−
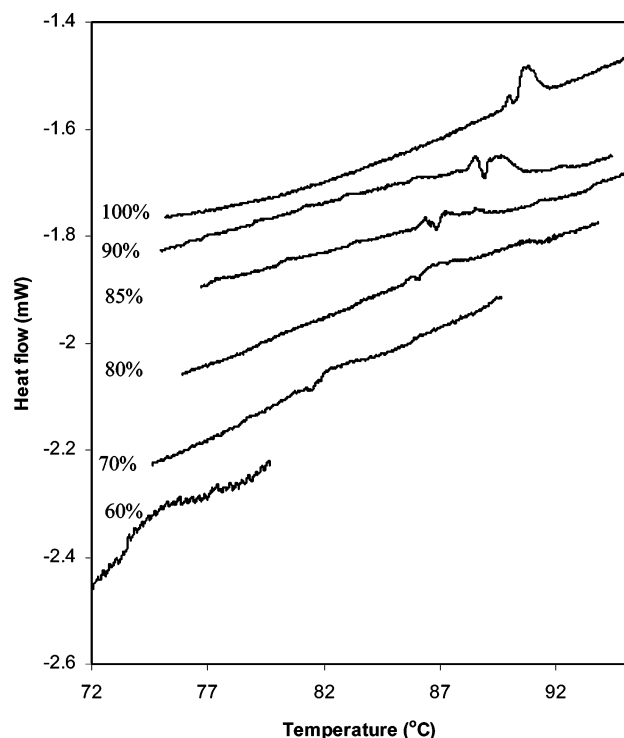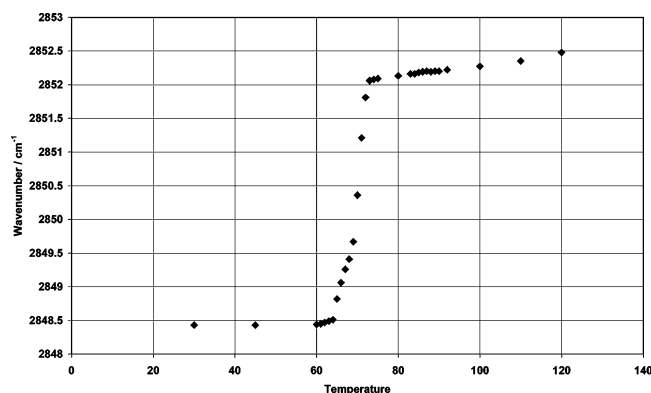
Stearic Acid and Triethanolamine Stearate

J. Phys. Chem. B, Vol. 109, No. 23, 2005 **11759**

Figure 10. DSC heating curves of stearic acid at different neutralizations at 0.1 °C/min scanning rate.

Figure 11. Shift of the CH_2 symmetric band, 2850 cm^{-1}, for 85% neutralized sample with increasing temperature.
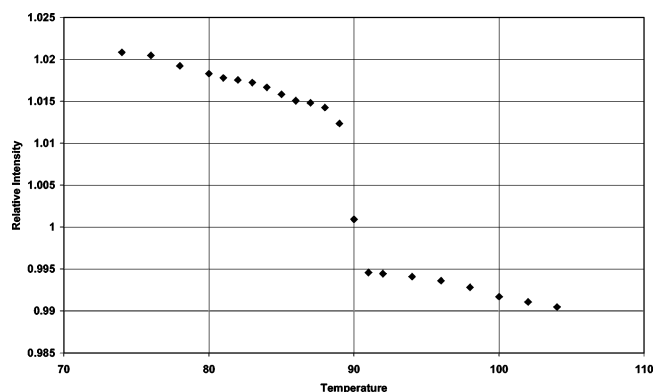

Figure 12. Plot of 1301 cm^{-1} band intensity relative to 1276 cm^{-1} band, with temperature for 85% neutralized sample.

neutralization sample is shown in Figure 12, with a sharp transition at 90 °C. Similar results were obtained for the other samples.[16]

3.5.2. FTIR of Headgroups Upon Heating. At room temperature, the acid carbonyl stretch is at approximately 1700 cm^{-1}, the soap carboxylate stretch is at 1530 cm^{-1}, and the acid−soap carboxylate is at 1575 cm^{-1} (see section 3.2). Upon melting, the acid carbonyl shifts upward to 1710 cm^{-1}. The soap carboxylate stretch also shows a shift upon melting, to 1560 cm^{-1}. When a mixed phase is heated, the carbonyl peak shows the same behavior as that for the pure acid and shifts to approximately 1710 cm^{-1}. At the same temperature, changes are also observed in the carboxylate region, with only one peak being present at 1560 cm^{-1}. The temperature of these transitions is the same as that assigned above to the acid−soap melting to the liquid crystal phase. The frequencies for the carbonyl and carboxylate after this transition are the same as those for acid and soap, respectively. So at this transition, the acid−soap complex actually breaks up into its constituent parts of soap and acid.

Therefore, by using a number of bands, one can observe the behavior of the different components with temperature, and the change that occurs can be identified. The temperature of all of the transitions can also be measured within one degree. These can then be plotted in a phase diagram that matches that obtained by DSC very well.[16] So a complete phase diagram can be obtained from the FTIR measurements giving not only the transition temperatures but also the species present and the state they are in. This is the first time a complete phase diagram of this type has been mapped by infrared.

3.6. Microscopy. The melting behavior of the samples with different neutralizations was also investigated using hot-stage microscopy with transmitted brightfield and polarized light.

The melting behaviors of the samples below 33% neutralization agree well with the DSC, X-ray, and IR results. There is one phase transition (birefringent solid to optically isotropic liquid) occurring for pure stearic acid and the acid−soap complex. For composition between stearic acid and the acid soap, one solid to liquid transition was generally seen and it was difficult to observe the melting temperature difference between stearic acid and the acid soap because the two crystals have very close melting temperatures.

At neutralizations above 33%, a more complicated melting behavior was observed. For example, the 85% neutralized sample melted partially to form a liquid phase at 65 °C on heating. This agrees well with the IR results shown in section 3.5, where the acid soap breaks up into acid and soap at approximately this temperature. The volume of the liquid phase
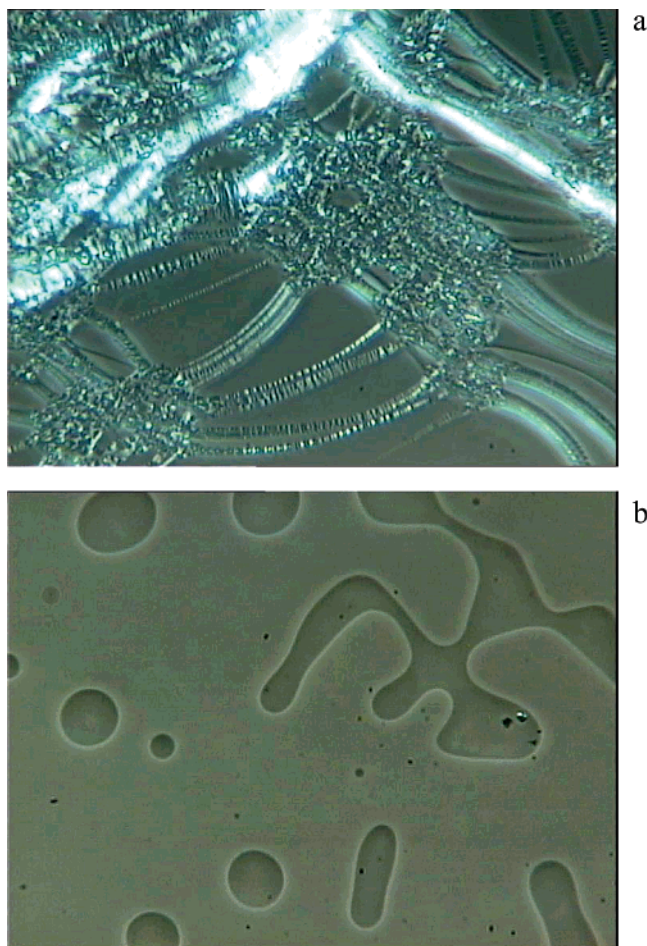
soap melting/break-up, as it is the minor component at this level of neutralization. The second larger transition at 70.5 °C is due to the soap melting. These assignments are confirmed by the headgroup behavior, see below. Similar results are observed with all of the samples, with the transitions observed being approximately proportional to the amount of each species present. The small transition at approximately 90 °C is due to the change to isotropic liquid. However this transition is seen more clearly in other modes, in particular, in modes originating from CH_2 wagging and bending modes. At room temperature, the series of bands arises from the wagging progression of the CH_2 groups in the trans conformation are seen.[23] When heated, the alkyl becomes disordered and this wagging progression gradually fades to be replaced by other bands due to different conformations then present in the alkyl chain; these are discussed and fully assigned elsewhere.[16] A ratio of the intensity of the two bands shows the transition to isotropic liquid sharply; they are the bands at 1301 cm^{-1} due to the CH_2 groups in the gauche trans gauche$'$ (gtg$'$) conformation[24] and the 1279 cm^{-1} band of a methylene wag.[20] A plot of the relative intensities for the 85%

Figure 13. Microscopy images of 100% neutralized stearic acid at different temperatures. Image width is 320 μm. a: 90 °C, polarized light; b: 95 °C, transmitted light.

Figure 14. Binary phase diagram of stearic acid and TEA stearate. a: stearic acid; as: acid soap; s: soap; l: isotropic liquid; l_c: liquid lamellar crystal.

increases and then decreases with further increasing of temperature. It seems that the liquid phase combines with the remaining solid phase to form a liquid lamellar phase during the melting of the solid phase at ca. 75 °C. A lamellar liquid crystal phase was observed under polarized light above this temperature. The liquid crystal phase started melting at 88.6 °C and a two-phase stage formed, which could be seen under normal transmitted light. The two-phase stage, similar to an emulsion with large droplets, ca. 20−50 μm in diameter, dispersed in a continuous liquid phase. The droplets coalesced with a further increase in temperature, and an isotropic liquid was formed at 92.4 °C.

The 100% neutralized sample also shows a similar melting behavior to the 85% sample. A small liquid phase formed at 65 °C and disappeared at around 73 °C. The solid crystal melted completely at 75.5 °C to form a lamellar liquid phase, see Figure 13a. A two-phase emulsion-like region also appeared between 94 °C and 96.2 °C, see Figure 13b. Above 96.2 °C, an isotropic phase formed. The formation of the liquid phase at 65 °C and also the two-phase region above 90 °C was not expected for a pure TEA soap. Because TEA and stearic acid are a weak base, $pK_a = 8$, and a weak acid, $pK_a = 4.8$, respectively, we expected that the neutralization reaction would not finish completely. This was confirmed by IR[16] and also reported in the literature.[8,9] The observation is explained by the existence of a small fraction, 2−3%, of stearic acid within the soap crystal at 100% neutralization.

3.7. The Binary Phase Diagram of Stearic Acid and TEA Stearate. The phase diagram of stearic acid and TEA stearate is drawn in Figure 14. It is based on the results obtained from
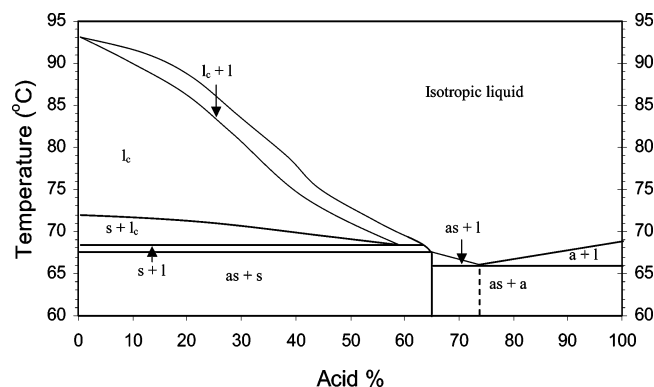
X-ray, DSC, microscopy, and FTIR techniques. The major phase transition temperatures plotted were obtained from the DSC peak temperatures measured at 1 °C/min.

The phase diagram shows that the acid−soap complex at a 2:1 ratio is formed between TEA stearate and stearic acid. A eutectic transition point occurs at about 25% neutralization when the melting temperature is 65.9 °C. The acid soap has a simple melting behavior from solid to liquid, and its melting temperature is about 3 °C lower than that of stearic acid. TEA soap (in absence of any acid−soap complex) melts to form a lamellar liquid crystalline phase at 71.7 °C, and the liquid crystal melts to form an isotropic liquid at 93 °C. Overall, the feature of this binary phase diagram looks very similar to that of the binary system of oleic acid and potassium oleate,[1,7] although the phase transition temperatures and the acid−soap ratio are different for the two systems. The phase transition temperatures and boundaries at neutralizations slightly above 33% are very close, and we could not discern them by DSC or by microscopy.

The resolution of the phase behavior of stearic acid and TEA soap is complicated by the closeness of the phase transition temperatures of the fatty acid, acid soap, and soap. We have used a number of complimentary techniques to determine the transition temperatures, sequence, and structural information and have extrapolated from the nonequilibrium experimental results to create the phase diagram. Because of the inherent high-temperature resolution of the DSC, from precision instrumentation, small sample size, and availability of the technique for many repeat measurements, this technique was used to determine the phase transition temperatures. The structural information available from X-ray data was mapped onto the DSC results. Optical microscopy was used to clarify more complicated areas of the phase diagram.

The phase diagram of TEA stearate and stearic acid shows significant differences from that of alkali stearate and stearic acid in terms of the phase transition temperature and the acid−soap complex ratio. The TEA system forms only one acid−soap complex at a 2 to 1 ratio, and the complex melts to form an isotropic liquid at a lower temperature than that of stearic acid. Alkaline systems can form a few acid−soap complexes with different stoichiometric ratios.[1,4,5] The melting temperature of alkaline acid soaps is significantly higher than that of the corresponding fatty acids.[1,2,5,6,7] The melting temperature and process of TEA soap are also significantly different from the alkali soap. First, TEA soap melts to form a lamellar liquid crystal at much a lower temperature than that of the alkaline soap.[1,2,5] The liquid crystal then melts into an isotropic liquid at ca. 93 °C; that is also significantly lower than that of alkaline soap. Alkali soap normally melts to an isotropic liquid at ca.

Stearic Acid and Triethanolamine Stearate

J. Phys. Chem. B, Vol. 109, No. 23, 2005 **11761**

300 °C. It was also observed that TEA soap goes through a simpler melting process, solid to lamellar liquid crystal to isotropic liquid, on heating, whereas alkali soaps go through a number of phase transitions, up to 8, to reach an isotropic liquid.[20]

The difference resulting from using TEA soap and acid soap is probably related to the size of the counterion headgroup and the crystalline structure formed as a consequence of that. This structure seems to significantly reduce the interactions between the headgroup as evident by the lower melting temperature and smaller melting enthalpy compared with alkali soaps. The large counterion was reported to be the main factor determining the unusual interaction and phase behavior between TEA stearate and water at room temperature.[8,9]

4. Conclusions

We describe comprehensive studies, for the first time, of the interactions of stearic acid and its soap neutralized with the organic base triethanolamine. A wide range of experimental methods was used to gain a thorough understanding of the system. The experimental results prove the formation of only one acid−soap complex with a fixed stoichiometric ratio of 2:1 between the acid and the soap. The acid−soap complex adopts a bilayer lamellar crystalline structure of 52.2-Å repeat distance. The soap crystal has a much shorter repeat distance of 32.6-Å layer structure. The melting temperature of the acid soap and the soap is very close to that of stearic acid, which is significantly lower than that of acid soaps and soaps made from alkali bases.

The introduction of a large size counterion in the crystalline structure contributes a great deal to the phase behavior and the interaction of the fatty acid and TEA soap. The large counterion group seems to weaken significantly the molecular interactions between the fatty acid and TEA soap, therefore lowering dramatically the melting temperature of the acid soap and soap and also the phase transition enthalpy. This work increases our understanding of the soap and acid soap knowledge that has been accumulated over one century based on alkali systems and provides a binary phase diagram of stearic acid and an amine soap. It also highlights an interesting area of interaction between the TEA neutralized system and water for future study.

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