Preparation and Characterization of Surface Active Erucic Acid Derivatives

Angela Jönsson*, **Jeanette Bokström**, **Ann-Charlotte Malmvik** and **Torbjörn Wärnheim**
Institute for Surface Chemistry, P.O. Box 5607, S-114 86 Stockholm, Sweden

Nonionic, cationic and anionic surfactants, derivatives of *cis*-13-docosenoic acid (erucic acid), have been prepared and characterized, and their performance has been evaluated and compared with the corresponding derivatives of fatty acids with shorter alkyl chain length.

Nonionic erucic acid ethoxylates give a solution behavior anticipated from the hydrophilic-lipophilic balance of the molecule; however, the increased molecular size as compared to ordinary surfactants results, e.g., in higher temperature stability of the surfactant aggregates. Anomalous solution behavior was found and investigated for anionic surfactants, triethanolammonium salts of erucic acid, and some shorter homologues. The effects are discussed in terms of the acid-base equilibria of the alkanolammonium counterion and the acid, together with effects due to the molecular size of the counterion.

KEY WORDS: **Alkanol amine, alkanolammonium carboxylates, erucic acid, phase equilibria, triethanol amine.**

Although fatty acids remain one of the major raw material sources for surfactants (1), several simple derivatives have not yet been fully characterized. As one example, solution phase studies of long chain fatty acid derivatives (>C20) are quite rare; a reason for this is the tendency for such compounds to have Krafft-points high above room-temperature, limiting their use to rather specific applications. However, by choosing branched or double bond-containing fatty acids, the Krafft-point can be considerably lowered by the destabilization of the crystalline state, while retaining a large hydrophobic volume of the surfactant molecule. Of course, in particular alkali salts (soaps) of most long chain fatty acids, including unsaturates such as erucic acid (C22:1, *cis*-13-docosenoic acid), are well-known (2). However, while carboxylates with an alkyl chain length up to C18 (stearate) or C18:1 (oleate) are standard model compounds (and technically common products), surfactants based on, e.g., erucic acid are, to the best of our knowledge, not commercially produced; also, available literature on such compounds is not very extensive (3).

Thus, in this study we have chosen to investigate the solution behavior of amphiphiles derived from erucic acid. Erucic acid is well-known for being a suspect arteriosclerosis agent (4)—rapeseed oil, previously often containing up to 50% C22:1, is due to successful plant breeding available more or less erucic acid free (<0.5%) (5). However, high erucic acid strains are still being cultivated, and it is possible to produce the acid on a commercial scale. This explorative study is aimed at studying the effects of the alkyl chain length for different relevant derivatives of erucic acid. In particular, we have investigated the differences in behavior due to the alkyl chain length.

EXPERIMENTAL PROCEDURES

Chemicals. Technical quality erucic acid (*cis*-13-docosenoic acid) (Fluka AG, Buchs, Switzerland, 90%; or Riedel-de-Haen AG, Selze, Germany, >90%), was used for the syntheses. The fatty acid compositions were analyzed according to standard procedures (Table 1). The melting point was 30°C (literature value for pure sample, 33.5°C) and the amount of unsaponifiables rather low; the acid was thus deemed sufficiently pure for our purposes. Erucic acid ethoxylates were obtained by reacting the acid chloride with large excess of polyethylene glycol with mean molecular weights of 300 and 600, respectively, corresponding to 7 and 14 ethoxy units. The surfactants are denoted $C_{22}EO_7$ and $C_{22}EO_{14}$, respectively. Erucyl ammonium chloride, $C_{22}NH_3Cl$, was obtained by reduction of erucyl amide with $LiAlH_4$. Amine soaps, i.e., triethanolamine salts of erucic (C_{22}), lauric (C_{12}) and caprylic (C_8) acid (denoted TEA-C_{22}, TEA-C_{12} and TEA-C_8, respectively), were prepared by mixing equal molar amounts of the amine and the acid in ethanol and evaporating the solvent.

Phase diagrams. Phase diagrams were prepared for the nonionic and anionic surfactants, according to standard procedures. Binary systems were studied by equilibrating samples in a thermostatted bath, followed by visual inspection for turbidity or anisotropy. Liquid crystalline phases were identified in a Reichert polarizing microscope (C. Reichert, Vienna, Austria) equipped with a hot stage. By raising and lowering the temperature at a suitable rate (3°C/min), the existence regions for the liquid crystalline phases could be determined. The fatty acid ethoxylates are sensitive to hydrolysis; measurements were made on freshly prepared solu-

TABLE 1

Fatty Acid Composition for Commercially Available Erucic Acid

Chainlength	Riedel-de-Haen	Fluka
<C20	0.2	0.8
C20	2.5	3.2
C22 (tot)	94.9	93.1
C22:1	92.5	89.9
C24	2.2	2.4
Unknowns	0.2	0.2
Unsaponifiables	1.4	1.9
Melting point	28–32°C	28.5–31.5°C

---

*To whom correspondence should be addressed.

tions. It should be noted, however, that, for example, measured cloud points changed with long time storage at elevated temperature.

Emulsions. Emulsions were prepared with the nonionic surfactants, using an Ultra Turrax homogenizer (Janke & Kunkel, Staufen, Germany) at 20°C, using maximum effect on 20 mL samples. The emulsions were inspected visually for stability after storage.

Surface tension measurements. Surface tension measurements were performed for the water-soluble nonionic and anionic surfactants using the de Noüy ring method at 20°C. The accuracy is estimated to ± 0.5 mJ/m^2.

Contact angle measurements. Cleaned glass surfaces were immersed into cationic surfactant solutions for 20 seconds, pulled out, rinsed by acetone and dried (6). Contact angles, obtained as the advancing contact angle, were measured on a Ramé-Hart goniometer (Ramé-Hart Inc., NJ).

RESULTS AND DISCUSSION

Erucic acid ethoxylates. Two different nonionic surfactants, erucic acid ethoxylates with varying hydrophilicity, $C_{22}EO_7$ and $C_{22}EO_{14}$, were characterized with respect to their amphiphilic properties. As a starting point, the binary phase diagrams with water were prepared (Fig. 1). $C_{22}EO_7$ is water insoluble at room temperature and forms a lamellar (D) phase melts into a solution phase, L_2, above 90°C. This increase in melting point for the D-phase compared to nonionics with similar hydrophilic-lipophilic balance (HLB), 10.5, but lower molecular weight is anticipated since the melting points of liquid crystalline phases increase with increasing molecular weight of the surfactant. Apart from that, the features of the phase diagram are very similar (7). In view of these similarities, it has not been deemed necessary to determine the phase equilibria in all details (e.g., the extension of the narrow two-phase regions between liquid crystalline phases and solution phases). $C_{22}EO_{14}$ is hydrophilic and water soluble up to 45 wt%, where a cubic (I) phase or a hexagonal (E) phase precipitates. Again, the higher temperature stability of the liquid crystalline phases is the only major feature which distinguishes $C_{22}EO_{14}$ from derivatives with lower molecular weight. $C_{22}EO_7$ has a cloud point below 0°C, and $C_{22}EO_{14}$ has one above 100°C (Table 2); however, their mixtures give cloud points in the intermediate temperature interval. Thus, mixtures with the appropriate HLB can be tailored (Fig. 2).

One anticipated advantage of using surfactants of a larger molecular size is an increase in solubilizing capacity (8)—thus, the formation of microemulsions was investigated in some detail. The phase behavior for the system $C_{22}EO_7$/water/hexadecane at varying temperatures is shown in Figure 3. Comparison with previous investigations of microemulsion formation with other surfactants with a similar HLB suggest an optimum solubilization temperature around 55°C for the system (9). The phase behavior revealed an optimum solubilization around 60°C, and further increasing the temperature did not increase the extension of the solution phase region towards the lower surfactant content. However, the microemulsion regions are not significantly more extensive than those obtained with smaller, balanced surfactants (9).

Emulsion stability was studied for the two ethoxylates together with different lipophilic components (alkane, aromate, triglyceride). However, the studies revealed no significant differences compared with lower molecular weight emulsifiers with C_{16-18}-chains. For example, $C_{22}EO_{14}$ gives stable emulsions with aromatic hydrocarbons at room temperature, as is predicted from considerations of the required HLB (9).

The main surfactant characteristics of the erucic acid ethoxylates can be predicted from considerations of the hydrophilic-lipophilic balance by itself, and the behavior is comparable to that of lower molecular weight fatty acids or fatty alcohol ethoxylates. There are some expected differences due to the increase in molecular weight—an increase in stability of ordered phases—but they seem slightly offset by the double bond, which affects the molecular packing in surfactant aggregates.

Erucyl ammonium chloride. A rapid check of the

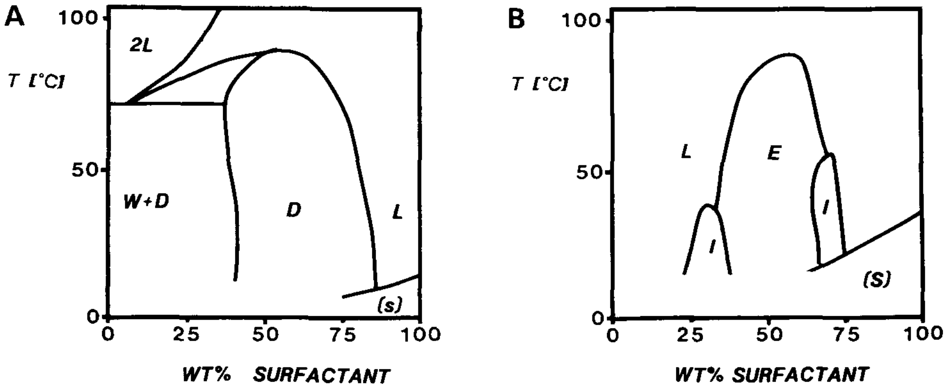

FIG. 1. a) Phase diagram for the system water/$C_{22}DO_7$. W denotes dilute aqueous phase; D, lamellar liquid crystalline phase; L, isotropic solution phase; and (s), solid surfactant. b) Phase diagram for the system water/$C_{22}EO_{14}$. L denotes solution phase; E, hexagonal liquid crystalline phase; I, cubic phases; and (s), solid surfactant.

TABLE 2

Cloud Points and Critical Micelle Concentration, CMC, (Where Applicable) for Two Erucic Acid Ethoxylates.

Surfactant	HLB	CMC [mM]	Cloudpoint [°C]	Area [Å^2]^a
$C_{22}EO_7$	10.5	—	69°C^c	—
$C_{22}EO_{14}$	13.5	0.002	63°C^b	50

[a] Area from surface tension measurements, slightly below CMC, using the Gibbs adsorption isotherm.

[b] One wt% surfactant in 10 wt% NaCl(aq).

[c] One wt% surfactant in 25 wt% butyldiglycol.

phase behavior of the cationic erucate derivative indicated no formation of a hexagonal liquid crystalline phase; instead a direct precipitation of a lamellar phase occurs at ca. 10 wt% surfactant. However, the amphiphilic behavior of cationic surfactants is particularly interesting due to their adsorption affinity onto negative surfaces. Therefore, $C_{22}NH_3Cl$ was investigated with respect to adsorption behavior and hydrophobizing capacity. The surfactant adsorbs to surfaces at low concentrations, which is revealed by Figure 4a. The stability ranges are shown for a dispersion of ground mica in different concentrations of $C_{22}NH_3Cl$ solutions. The mica dispersion is stable in pure water due to double layer forces between the negatively charged basal planes of the dispersed mineral. These charges are gradually neutralized by adsorption of surfactant which finally destabilizes the dispersion. At higher concentrations of surfactant the dispersion becomes stable again due to the formation of a bilayer of surfactant.

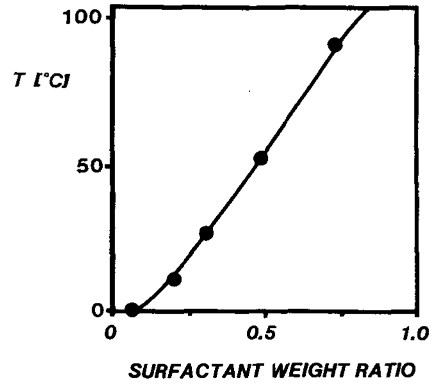

FIG. 2. The shift in cloud point for a 1 wt% surfactant solution in water when changing the surfactant weight ratio W = $C_{22}EO_{14}$/($C_{22}EO_7$ + $C_{22}EO_{14}$)) from W = 0 to W = 1.

A more quantitative investigation of the hydrophobing capacity was performed for a series of surfactants—C_8NH_3Cl, $C_{12}NH_3Cl$ and $C_{22}NH_3Cl$. The surfactants were adsorped from solution onto glass surfaces and the effect on the advancing contact angle, θ, for water was determined over a wide concentration range (Fig. 4b). The comparison is particularly relevant since the adsorption behavior of short and medium chain alkyl ammonium chlorides has been carefully investigated in a number of studies (6). Up to the millimolar range, there is no visible effect on the contact angle for C_8NH_3Cl, suggesting no adsorption. For $C_{12}NH_3Cl$, there is an effect, particularly at high concentrations. For $C_{22}NH_3Cl$, the surface becomes more hydrophobic at concentrations of 0.1 mM (however, $\theta < 60°$), while at higher concentrations the decrease in the contact angle reveals the formation of a bilayer, the surface becomes completely hydrophilic. This occurs in the same concentration regions as with the mica surface.

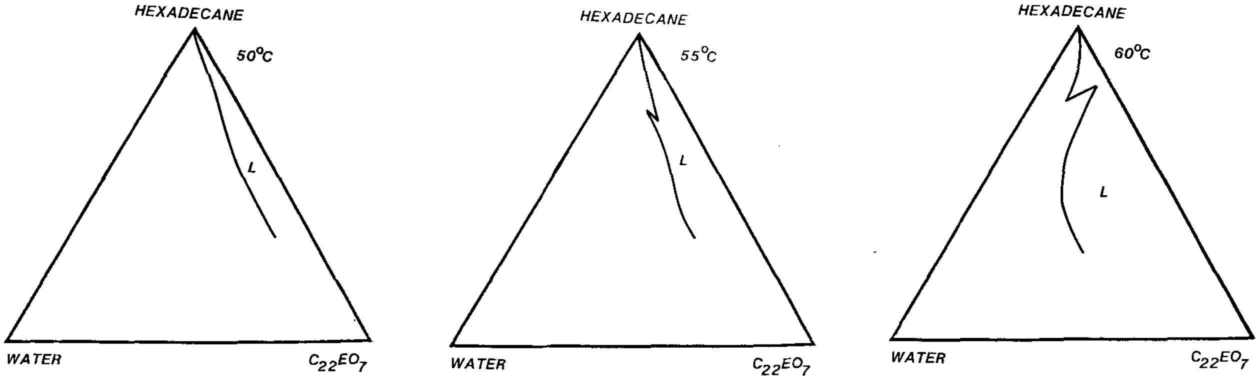

FIG. 3. Microemulsions formed in the system water/hexadecane/$C_{22}EO_7$. Only microemulsion (L) regions are shown at three different temperatures.

Erucates. Alkali metal salts, soaps, are well characterized even for long chain fatty acids, although the number of reports for erucates is small. The detailed phase behavior of water/alkali erucate systems has not been reported in the literature. A screening of the phase diagram of the water/sodium erucate system showed a stronger tendency to form lamellar phases than, e.g., for the corresponding oleate or stearate [accurate phase diagrams for these compounds are available (10)]. The Krafft-point for sodium erucate is approximately 60°C. A lamellar phase is stable already at 30 wt% surfactant, as compared to 40 wt% for oleate or stearate (10). No extensive formation of a hexagonal phase occurred.

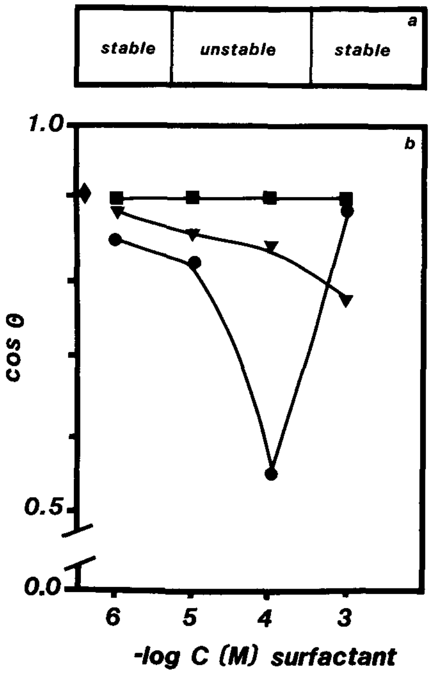

FIG. 4. a) Stability region for a mica dispersion in equilibrium with $C_{22}NH_3Cl$ solutions of different concentrations (see scale of Fig. 4b). b) Contact angle for water drop on a glass surface contacted with C_xNH_3Cl solutions of different concentrations. (■), C_8NH_3Cl; (▼), $C_{12}NH_3Cl$; and (●), $C_{22}NH_3Cl$.

We have also prepared and characterized triethanolammonium carboxylates, as with TEA-C_{22}. For example, a study of such compounds with respect to phase behavior and solution structure is relevant not only with respect to the chain length dependence emphasized in this study, but also with respect to a general question on the effect of alkanolamine as a counterion (or a constituent) in fatty acid systems. Alkanolamines have extensive practical use both in surfactants (amine soaps) and as additives to fatty acid/soap systems (1). The depression of the Krafft-point (evident from Figs. 5 and 6) that occurs for alkanolammonium carboxylates compared to normal soaps is of particular interest for long chain fatty acids. Recent studies have been provided by Friberg *et al.* (11,12), who characterized the phase behavior in a number of systems containing triethanol ammonium oleate. It was noted that there might be only a partial neutralization of the acid due to the equilibrium between carboxylic acid/carboxylate, but that specific interactions between the acid and the amine were discussed as well (11). (The designation triethanol ammonium carboxylates is used without any inference on the proportion between acid/soap in solution).

In Figure 5 the binary phase diagrams with water are shown for TEA-C_8, TEA-C_{12} and TEA-C_{22}. The water/TEA-C_8 phase diagram (Fig. 5a) is essentially featureless. In contrast to the behavior of the corresponding alkali soaps, no liquid crystalline phases are formed. There is a very thin miscibility gap around 3–5 wt% surfactant. This region contains two liquids phases in equilibrium. An increase in the extension of the solution phase compared to normal C_{12} soaps is found in the water/TEA-C_{12} phase diagram (Fig. 5b); a hexagonal phase becomes stable at 50 wt% surfactant at room temperature, which is a considerably higher concentration then, for example, with NaC_{12}. A miscibility gap occurs at low surfactant concentration, 0.1–7 wt%. The composition of the separated phases varies with concentration. At slightly higher concentrations of surfactant, the system displays a phase separation with increasing temperature. For instance, a 10 wt% TEA-

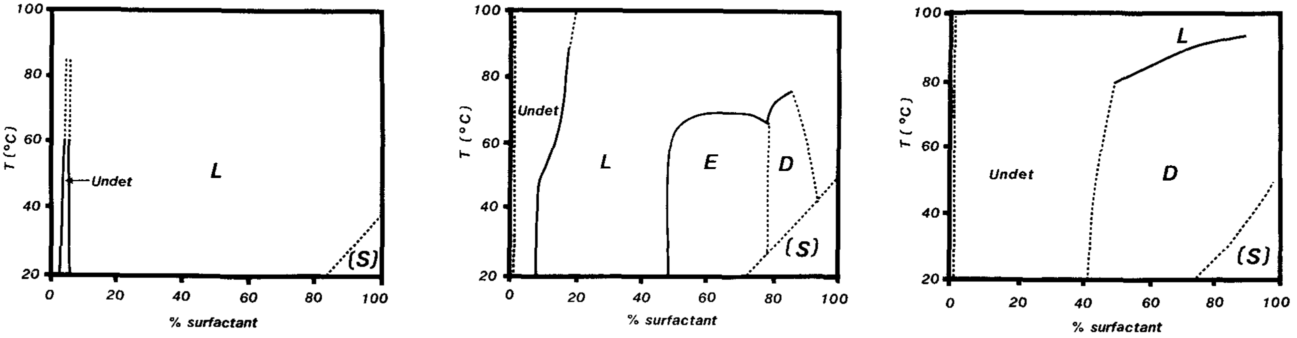

FIG. 5. Phase diagrams for systems containing water and fatty acid:triethanolamine, 1:1 (mole:mole), TEA-C_x, with different alkyl chain length. a), TEA-C_8; b) TEA-C_{12}; and c), TEA-C_{22}. W denotes very dilute aqueous solution; L, solution phase; E, hexagonal phase; D, lamellar phase; and (s), solid surfactant. "Undet" denotes multiphase regions as explained in the text.

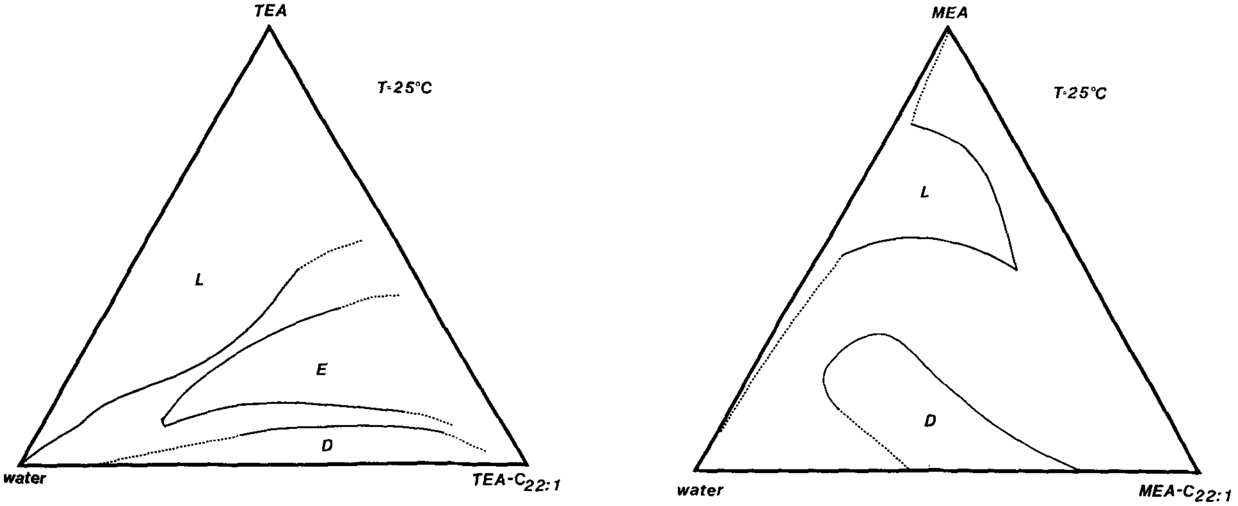

FIG. 6. Notations as in Figure 5. a) Phase diagram for the system water/TEA-C_{22}/TEA at 25°C. b) Phase diagram for the system water/MEA-C_{22}/MEA at 25°C.

C_{12} solution is stable at room temperature, but phase separates into two liquid phases at 50°C. Finally, for water/TEA-C_{22}, the surfactant directly precipitates to a lamellar phase at low concentrations in water (Fig. 5c). The miscibility gap seems solely to consist of an aqueous phase, dilute in surfactant, in equilibrium with the lamellar phase. While an increase in alkyl chain length for a homologous series of surfactants leads to a larger tendency to form lamellae (10), this tendency is normally not so evident as for the erucates. Thus, there are two anomalies to take into account—the occurrence of miscibility gaps and a pattern for formation of liquid crystalline phases which deviates from that normally encountered for soaps.

The miscibility gaps of the components can most easily be explained by the assumption that the neutralization in solution of the acid is only partial, since the alkanolamine is not a sufficiently strong base. Thus, the binary system of water/TEA-C_x is in reality a ternary system, acid + TEA/soap/water (10,11). Assuming a distribution between acid and salt-form, this could explain the miscibility gaps. As a first approximation, we can assume that undissociated acid and excess TEA behaves as excess acid. This should result in a miscibility gap in the water-rich region, while the lamellar phase becomes stable at higher surfactant concentration (10), since this is known to occur in ternary systems water/soap/acid even at low ratios of acid/soap. The extensions of the lamellar phase increase and those of the solution phase decrease with increasing surfactant alkyl chain length (Fig. 5) in agreement with the behavior of the ternary systems (10). We have recently shown (13) that with monoethanolamine (MEA) as counterion, the phase behavior becomes more similar to that of alkali soaps, in agreement with the acid-base equilibria. MEA is a stronger base than TEA, which results in a higher fraction of charged components at similar concentrations.

However, not all features of phase diagrams are explicable in terms of the acid-base distribution. An effect due to counterion size can be illuminated by studying the ternary phase diagrams water/TEA-C_{22}/TEA and water/MEA-C_{22}/MEA, as shown in Figure 6. Adding excess TEA to the lamellar phase in the water/TEA-C_{22} system results in the precipitation of a hexagonal phase with higher curvature, which should be due to the increased amount of the bulky TEA at the aggregate surface (Fig. 6a). Adding excess of MEA with a smaller molecular size to the water/MEA-C_{22} system, however, does not affect the system similarly—no hexagonal phase is formed (Fig. 6b). The trend is opposite to that anticipated from acid-base equilibrium; MEA is a slightly stronger base than TEA, which should lead to a more extensive acid dissociation, a higher surface charge and a preference for higher curvature aggregates. Thus, this must be explained as a steric disordering due to the larger size of TEA as compared to MEA.

We have characterized the behavior of surface active erucic acid derivatives and traced out the importance of the alkyl chain length by comparison with derivatives of shorter chain length. It is clear that there are substantial differences compared with, for instance, C_{12}-derivatives, but the differences become less marked or cease to exist when comparing them to C_{18}-derivatives. The differences are, of course, proportional to the relative change in alkyl chain length; such effects do gradually become less drastic.

Another factor of importance is the double bond in the erucic acid alkyl chain which has a large influence on the chain packing, destabilizing ordered structures. This is advantageous for most applications since it lowers the Krafft-point, on the other hand, it will also affect the chain packing in surfactant aggregates with fluid hydrocarbon chains, such as lamellar phases or close packed, adsorbed, surfactant layers. A further lowering of the Krafft-point is obtained by using alkanolamines as counterions.

ACKNOWLEDGMENT

This work was financially supported by a grant from Stiftelsen Karlshamns Forskning (Karlshamn Research Foundation). We thank Jari Alander, Karlshamns AB, for arranging the fatty acid analysis and both he and Per Stenius for helpful comments.

REFERENCES

1. Falbe, J. (ed.), *Surfactants in Consumer Products,* Springer Verlag, Heidelberg, 1987.
2. Websky, K., *Jahrl. Fortschritt Chem.* 444 (1953).
3. Lowe, E.S., *Manufact. Chem. 56:*61 (1985).
4. Johnson, S.P., *Fd. Cosmet. Toxicol. 16:*635 (1978).
5. Appelquist, L.Å., and R. Ohlson, *Rapeseed,* Elsevier, Amsterdam, 1972.
6. Herder, P., Thesis, Royal Institute for Technology, Stockholm, 1988.
7. Mitchell, D.J., G.J.T. Tiddy, L. Waring, T. Bostock and M.P. MacDonald, *J.C.S. Faraday Trans. 79:*975 (1983).
8. Shinoda, K., and H. Kunieda, *J. Colloid Interface Sci. 42:*381 (1973).
9. Shinoda, K., and S. Friberg, *Emulsions and Solubilization,* Wiley-Interscience, New York, 1986.
10. Ekwall, P., *Adv. Liq. Cryst. 1:*1 (1975).
11. Friberg, S., P. Liang, F.E. Lockwood and M. Tadros, *J. Phys. Chem. 88:*1045 (1984).
12. Friberg, S., and D.W. Osborne, *J. Am. Oil Chem. Soc. 63:*123 (1986).
13. Wärnheim, T., and A. Jönsson, *J. Colloid Interface Sci.,* in press.

[Received July 19, 1989; accepted June 7, 1990]