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Selective Amidation of Fatty Methyl Esters with N-(2-Aminoethyl)-Ethanolamine Under Base Catalysis

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ABSTRACT

The reaction of N-(2-aminoethyl)-ethanolamine (AEEA) with saturated fatty methyl esters derived from coconut oil occurs under noncatalyzed conditions to yield principally N-(2-hydroxyethylamino)-ethyl fatty amide, *1*, derived from the condensation of the primary amine moiety of AEEA with the methyl ester. In the presence of 0.25 wt % sodium methoxide at low reaction temperatures (<90 C), 2 carboxamides are formed, the secondary monoamide, *1* and also the tertiary monoamide, N-(2-aminoethyl)-N-(2-hydroxyethyl) fatty amide, *2*. As this mixture of secondary and tertiary monoamides is heated to higher reaction temperatures (>120 C), the concentration of secondary monoamide *1* increases with a concomitant decrease in tertiary monoamide *2*. As the reaction time is increased at the elevated temperature, the tertiary monoamide continues to disappear. Increasing the base concentration to 2.5 wt % sodium methoxide, promotes selective formation of amide *2* at low temperature. The results constitute evidence that at least 2 mechanisms are operating in fatty methyl ester amidations with AEEA and provide a classic example of thermodynamic vs kinetic control. Because amides *1* and *2* are intermediates to imidazoline amphoteric surfactants (powerful detergents, wetting agents, emulsifiers and so forth), knowledge of the reaction mechanisms in operation during the condensation of fatty methyl esters with AEEA will permit better understanding of the resultant products and the related processing conditions.

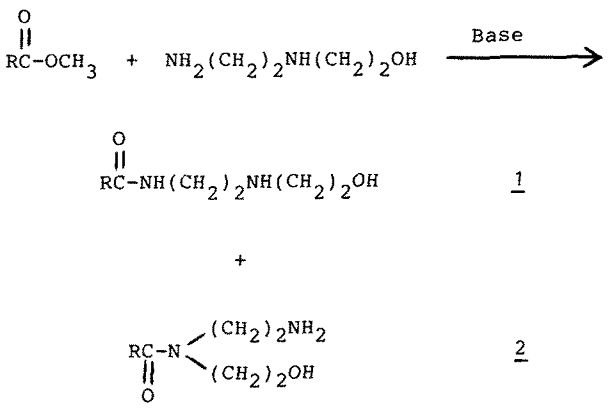
INTRODUCTION

The reactions of carboxylic esters with amines to form carboxyamides have been studied extensively (1-6). Careful kinetic research (5,6) has shown such reactions to be susceptible to base catalysis. Alkoxide catalysis had been used extensively by the fat industry, as early as 1949 (7), to accelerate the aminolysis of methyl esters and of triglycerides to mono- and diethanolamides (8-10). A number of preparative studies of the reaction of amines and esters, using sodium methoxide as the catalyst, showed that amide formation occurred rapidly at high reaction temperatures (11,12), but very slowly at room temperature (13). Furthermore, in the absence of any catalyst, extremely high reaction temperatures (150-250 C) are often necessary to convert esters to amides. Even under extreme conditions, however, only partial conversion could be achieved (14,15).

The reaction of fatty esters with N-(2-aminoethyl)-ethanolamine (AEEA) leads to fatty amides (16,17) that are intermediates to imidazoline amphoterics (18). The pathway to imidazoline formation occurs in 2 stages; amidation, followed by ring closure. The reaction of fatty esters with AEEA is not straightforward. Principally, 2 monoamides may form (Scheme 1).

The secondary monoamide, *1*, results from condensation of the primary amine moiety with the carboxylic ester, whereas the tertiary monoamide, *2*, results from secondary amine condensation. Chakrabarti (19,20) reported that initially, tertiary amide *2* was formed, followed by slow, thermally induced rearrangement to amide *1*.

The purpose of this investigation was: (a) to reevaluate the sodium methoxide catalyzed reaction of AEEA with



SCHEME 1

methyl esters; (b) to relate rate quantitatively to both temperature and catalyst concentration in order to permit approximate predictions of rate over a variety of operating conditions; (c) to contribute further understanding to the general mechanism of amidation reactions by proposing an empirically derived mechanism accounting for selective amidation of fatty methyl esters with N-(2-aminoethyl)-ethanolamine.

EXPERIMENTAL PROCEDURES

Materials

Methyl laurate was a commercial grade, purified so that purity, as determined by gas chromatography (GC), exceeded 99%. N-(2-aminoethyl)-ethanolamine was obtained from Union Carbide, New York, NY, and was freshly distilled for each experiment. Sodium methoxide was used as a 25 wt % solution in methanol.

Anhydrous methanol was obtained from Baker Chemicals, Phillipsburg, NJ. Commercial grade 2,4-pentanedione was purchased from Pfaltz and Bauer, Inc., Flushing, NY. It was distilled under atmospheric pressure and at 3:1 reflux, using a column having 26.0 mL of the redistilled pentanedione to 1 L with the freshly distilled pyridine.

Sodium methoxide was used as a 0.5 N solution in pyridine. A 3 N solution of sodium methoxide was prepared by dissolving 103 g dry sodium methoxide in sufficient methanol to make a 1 L solution. A 167 mL volume of the 3 N sodium methoxide and 40 mL of methanol was transferred to a 1 L volumetric flask and diluted to volume with redistilled pyridine. These solutions were standardized against benzoic acid with pyridine as solvent and thymolphthalein indicator, which was 1% solution in pyridine.

Methods

Amidation. A reaction mixture containing 107 g (0.5 mol) methyl laurate and 57 g (0.55 mol) N-(2-aminoethyl)-ethanolamine was heated to 20 C below the reaction temperature to be studied with vigorous agitation under distillation conditions. An exact quantity of a 25 wt % sodium methoxide solution was added all at once. The reaction temperature rose to the desired level and was maintained for the duration of the reaction. Aliquots were withdrawn after 5 min, 15 min, 30 min and 60 min of reaction. Each aliquot was chilled rapidly and hydrolyzed to destroy soap and catalyst.

Ester value determinations. Unreacted methyl ester and product were extracted with petroleum ether (3 × 25 mL) and the petroleum ether extracts evaporated to dryness. To determine ester remaining, the petroleum ether extract was saponified by refluxing with 1 N alcoholic potassium hydroxide for 1 hour. Hydrolysis of both secondary and tertiary amides was found to be negligible.

Determination of primary amine value (22). Exactly 10 mL of the 2.5 N pentanedione reagent was added to each of 2, 250 mL glass-stoppered Erlenmeyer flasks with a pipette. One flask was used as a blank. Into the other flask 10.0 meq of sample was introduced. Both sample and blank were allowed to stand at room temperature for 60 min. To each flask 1 mL of thymolphthalein indicator was added and titrated with standard 0.5 N sodium methoxide/pyridine solution until the first permanent blue color appeared. The difference between blank and sample was a measure of primary amine.

Synthesis of tertiary amide 2. A reaction mixture containing 107 g (0.5 mol) of methyl laurate, 57 g (0.55 mol) of AEEA and 10 g (2.5 wt % of ester) of a 25 wt % sodium methoxide solution was heated to 90 C under 30 mm Hg pressure for 30 min, during which methanol was rapidly removed, affording a clear and homogeneous liquid. IR analysis (film): 1720 cm^{-1} (COOMe) minor and 1660 cm^{-1} $(\underset{\underset{O}{\|}}{C}{-}NR_2)$ major.

No N—H bending was observed. Titration of the product for primary amine content gave 3.41 meq/g (theoretical value 3.50 meq/g).

Synthesis of secondary amide 1. The reaction mixture, as described above, containing 95% amide, was heated to 120 C under 30 mm Hg pressure for an additional 60 min. IR analysis (film): N—H stretch at 3290 cm^{-1}; OH stretch at 3260 cm^{-1}; amide-I at 1638 cm^{-1}; N—H bend at 1556 cm^{-1}; C=N stretch at 1600 cm^{-1} (small imidazoline contribution).

Titration of the product for primary amine content gave 0.1 meq/g (theoretical value 0.0 meq/g).

RESULTS

Kinetic Study

Throughout this particular investigation, the molar ratio of amine to ester was fixed at 1.1:1.0, and only catalyst concentration and reaction temperature were varied. In the absence of catalyst, an insignificant amount of amide was formed, and this was observed only after 3 hours at 120 C. Typical conversion profiles are shown in Figures 1, 2 and 3, representing the extent of amide formation at 60 C, 90 C and 120 C, with varying catalyst concentration. Percentage of conversion was calculated by employing equation 1:

$$\%\ \text{Conversion}_t = \frac{(\text{Original EV} - \text{Experimental EV}_t) \times 100}{\text{Original EV}} \quad [1]$$

where EV = ester value (meq/gm), and t = reaction time (minutes).

Figure 1 shows that at low reaction temperature (60 C), even with 2.5 wt % NaOCH$_3$, only 40% product yield was observed after 1 hour. However, at 90 C (Fig. 2), we observed a large rate increase when the catalyst concentration was increased 5-fold (0.25-1.25 wt %). After 1 hour, only 28% conversion was found with 0.25 wt % catalyst compared with 82% conversion with 1.25 wt % catalyst. No appreciable rate enhancement was found when the catalyst concentration was doubled from 1.25 to 2.5 wt %. Percent conversions vs time curves at 120 C (Fig. 3) again show a large rate increase at the higher catalyst concentrations. But again, no appreciable rate enhancement was detected when the reaction temperature was increased from 90 C to 120 C.

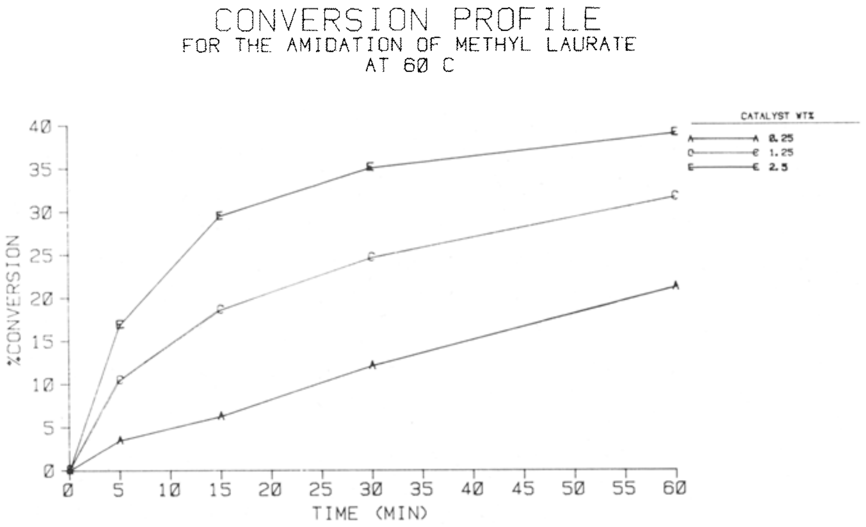


FIG. 1. Conversion profile for the amidation of methyl laurate at 60 C.

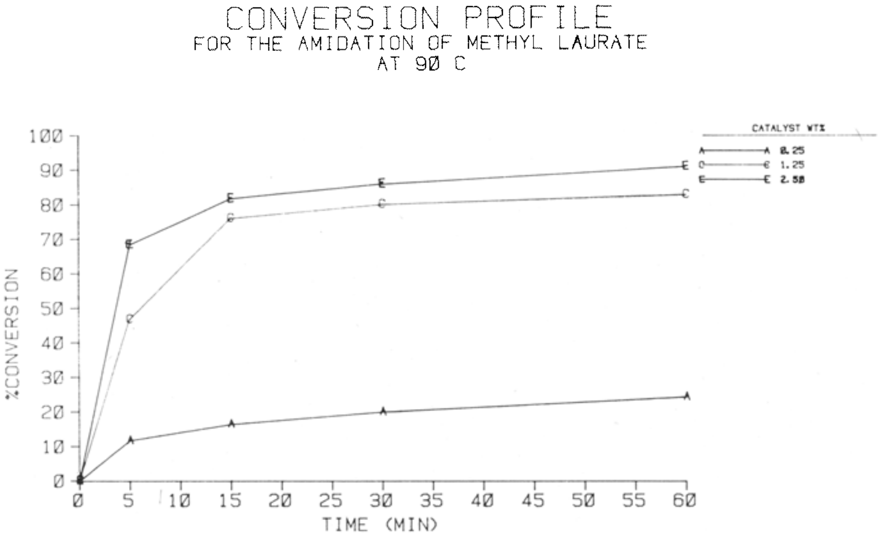


FIG. 2. Conversion profile for the amidation of methyl laurate at 90 C.

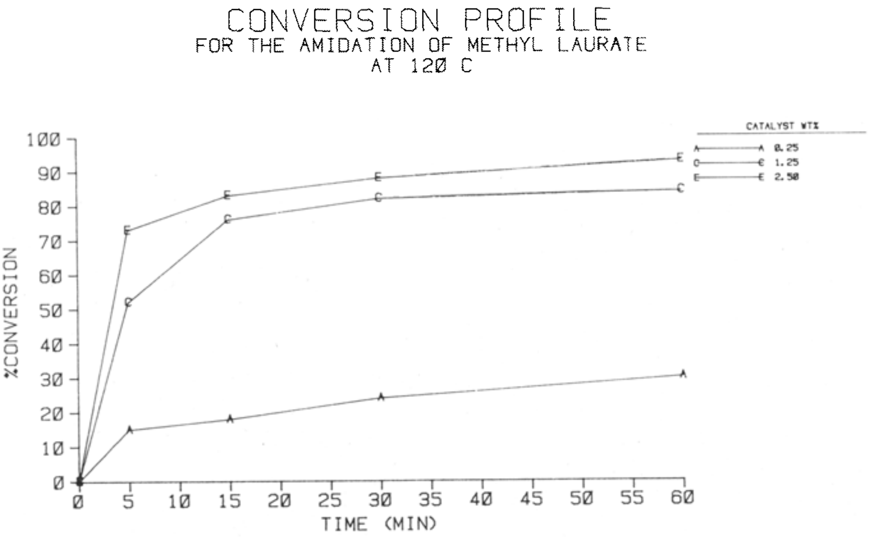


FIG. 3. Conversion profile for the amidation of methyl laurate at 120 C.

This effect is more clearly illustrated in graphical form in Figure 4. The kinetic data are plotted as percentage of conversion vs reaction time, with fixed catalyst concentration (2.5 wt %), and varying reaction temperature. As shown in Figure 4, after 5 min, only 15% amide was formed at 60 C. At 90 C, 68% conversion was observed, which was a 4.5-fold rate enhancement. At 120 C, 76% conversion was observed after 5 minutes.

The data within the first 15 minutes from Figures 1, 2 and 3 were evaluated by the least squares procedure and a correlation coefficient was determined for each slope. The data are graphically depicted in Figures 6, 7 and 8. Of particular significance is the virtual agreement in the average reaction velocity between experiments performed at 90 C and 120 C. Clearly, within the first 15 minutes, no advantage was observed when the reaction temperature was

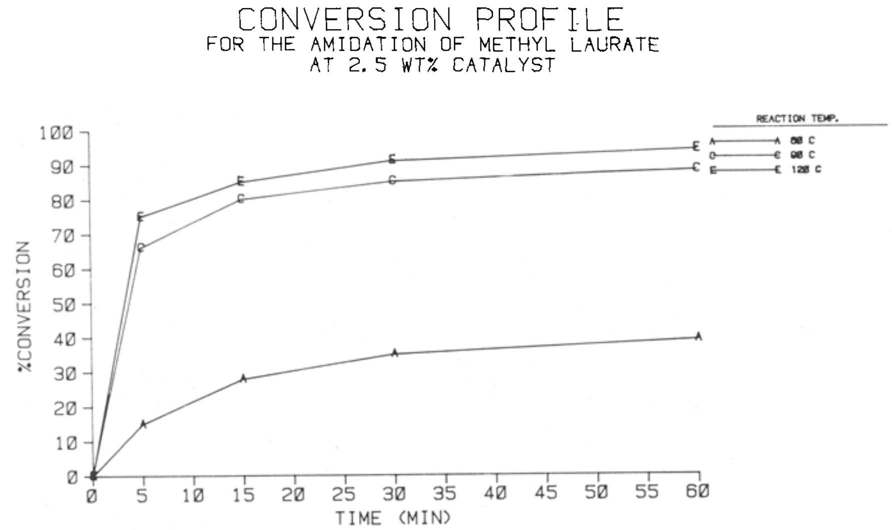


FIG. 4. Conversion profile for the amidation of methyl laurate at 2.5 wt % catalyst.

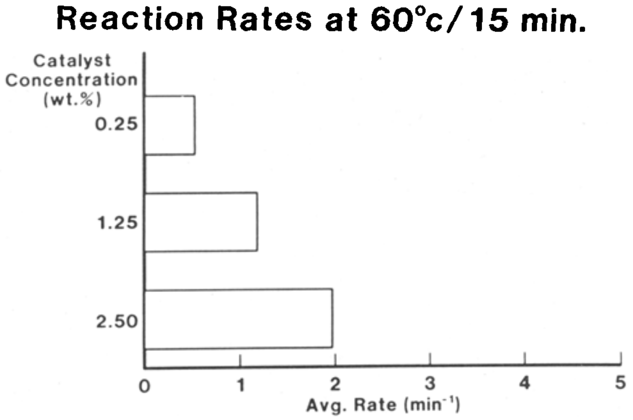


FIG. 6. Reaction rates at 60 C/15 min.

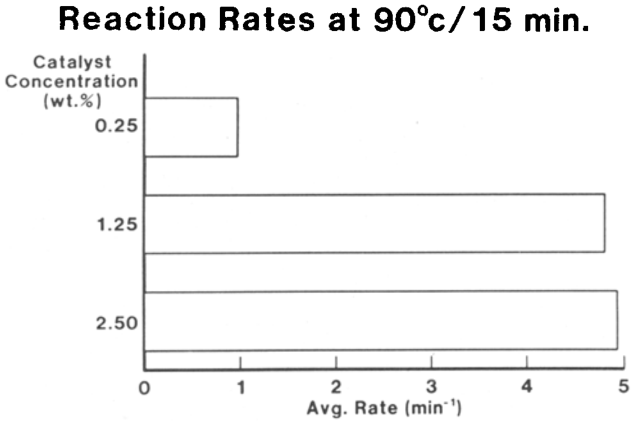


FIG. 7. Reaction rates at 90 C/15 min.

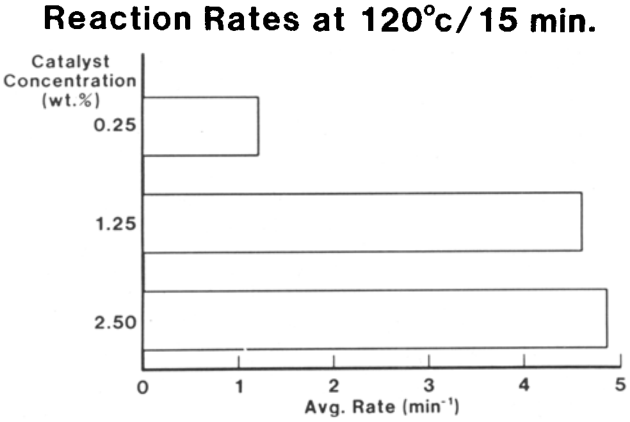


FIG. 8. Reaction rates at 120 C/15 min.

greater than 90 C. Although not tabulated, a good agreement in reaction velocity was also observed between 90 C and 120 C, even after 30 min. In relative terms, however, the overall amide yield after 1 hour was somewhat greater for experiments conducted at 120 C at all catalyst concentrations.

Figure 5 graphically illustrates the relationship between percentage of conversion and catalyst concentration during the first 60 min at varying temperatures. At low catalyst concentration, 0.25 wt %, a change in reaction temperature had little effect on the extent of product formation. A 5-fold increase in catalyst concentration clearly demonstrated the significance of reaction temperature. (As mentioned vide supra, percentage of conversions were determined after 60 min reaction time.) Using 1.25 wt % sodium methoxide, a large difference in reaction rate was observed between 60 C and 90 C. However, no appreciable increase in product yield was observed when the reaction temperature was raised from 90 C to 120 C.

Thus, the most effective reaction temperature, as deduced from the experimental data, was found to be 90 C. In addition, no appreciable increase in reaction velocity was observed when the catalyst concentration was greater than 1.25 wt %. Consequently, this appears to be the preferred concentration, and greater catalyst concentrations only lead to added costs.

Product Study

In addition to following the progress of product formation by saponification of the ester remaining, the reaction was monitored by infrared (IR) spectroscopy. Specifically, the disappearance of the methyl ester carbonyl stretch at 1720 cm^{-1} was followed simultaneously by the appearance of amide stretching vibrations. The secondary amide, *1*, could be distinguished from the tertiary amide, *2*, by observing the presence or absence of the amide bands associated with monosubstituted amides. At a catalyst concentration of 2.5 wt % at 90 C, only 1 amide band was observed in the IR spectrum, 1660 cm^{-1}. As the temperature was increased, we observed the appearance of a broad amide band at 1660-1620 cm^{-1} and a small N–H bending vibration at 1556 cm^{-1}. As the reaction temperature was raised to 120 C, the broad amide band shifted to a sharp frequency at 1638 cm^{-1} and a moderate band at 1556 cm^{-1}. This phenomenon suggested the presence of 2 amides at low temperature that were converted into one as the temperature was elevated.

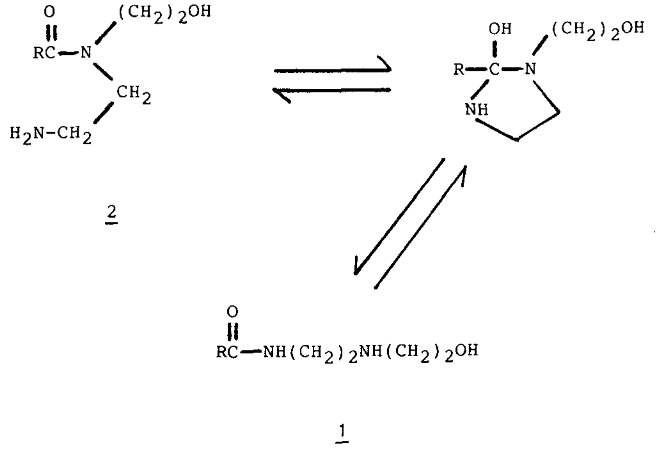
DISCUSSION

Data from the kinetic study clearly showed that no appreciable rate enhancement was observed when the reaction temperature was increased from 90 C to 120 C at higher catalyst concentrations. Yet, spectroscopic data indicated that at least 2 different species were formed, depending on the reaction temperature. Thus, I concluded that initially the tertiary amide *2* is formed and rearranges to the more thermodynamically stable amide *1* at elevated temperatures. This isomerization is depicted in Scheme 2.

Intramolecular attack of the carbonyl moiety by the free amino function of amide *2* is quite likely because the transition state leading to the cyclization is 5-membered and thus thermodynamically favored.

Furthermore, decyclization to afford amide *1* is favored because *1* is the thermodynamically more stable product. Hence, increasing the catalyst concentration would not be expected to favor amide *1*, as observed from the kinetic data.

I also observed by IR spectroscopy that, as the reaction mixture was kept at 120 C for prolonged periods (>60 min),



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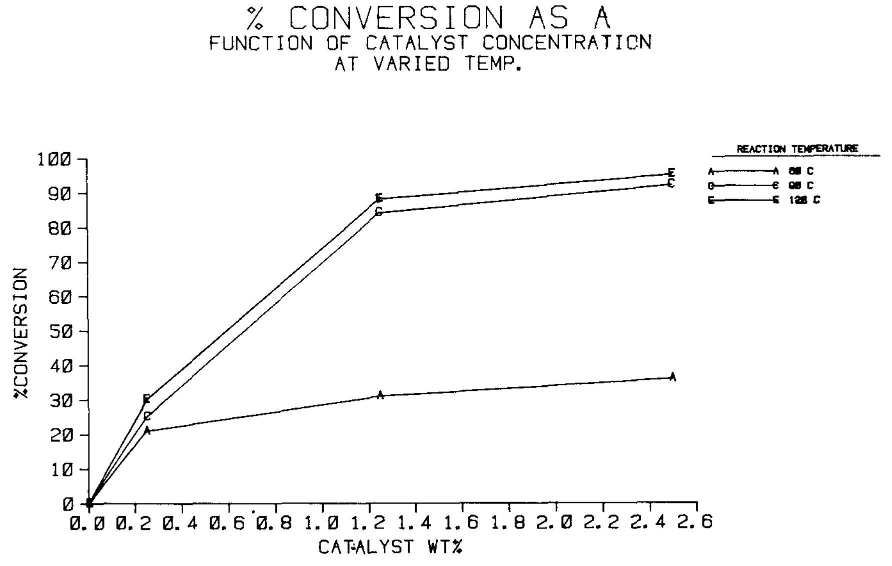

FIG. 5. Percentage of conversion as a function of catalyst concentration at varied temperatures.

a new frequency appeared at 1600 cm^{-1}. This band is associated with the C=N stretch of the cycloimidinium system, formed as a result of cyclization and loss of 1 molecule of water. This is depicted in Scheme 3.

Contrary to the reported (21) formation of the imidazoline system from either amide, *1* or *2*, the data show that the imidazoline system is derived mainly from amide *1*, because amide *1* is the predominant form at the temperature required for imidazoline formation.

Although direct aminolysis by either 1° or 2° amine would lead to amides *1* and *2*, respectively, under basic catalysis the initial reaction products consist of a mixture of new ester *3*, amide *1* and amide *2*. The composition of this mixture is determined by the kinetics of the various reactions. This discussion will focus on the formation of ester *3*.

The initial complex of AEEA with the methyl ester is similar to reactions of esters with ethanolamines. Namely, proton abstraction of the hydroxyl group of AEEA by the strongly basic methoxide ion would lead to alkoxide ion formation and subsequent transesterification of the methyl ester (11) to afford new ester *3*. The acyl moiety of an ethanolamide is known to undergo rapid migration from the nitrogen atom to the oxygen atom under strong acid conditions and reverse migration will occur from the oxygen atom to the nitrogen atom under basic catalysis (23,24). Therefore, in this system, transesterification is followed by rapid rearrangement under basic catalysis, producing amide *2*. A complete mechanistic scheme accounting for the experimental findings is delineated in Scheme 4.

As shown in the mechanistic scheme, the imidazoline system can be derived from both amides *1* and *2*. When the kinetics favor new ester formation, amide *2* is the kinetically controlled product. As the reaction temperature is increased, the thermodynamically controlled products, amide *1* and imidazoline, are produced.

The imidazoline-type transition state, *C*, either decyclizes to the secondary amide, *1*, or loses 1 mol of water to afford the imidazoline system. Because the reverse of reaction f would lead to the thermodynamically less stable amide *2*, at higher reaction temperatures the equilibrium is shifted toward intermediate *C* formation. In separate experiments, researchers observed that increasing the reaction temperature to 180 C accelerated reaction h and thus increased the yield of imidazoline (25).

The experimental results suggest that reactions a-e are kinetically controlled and thus dependent on catalyst concentration. Reactions f-h are thermodynamically controlled, independent of catalyst concentration and dependent only on reaction temperature.

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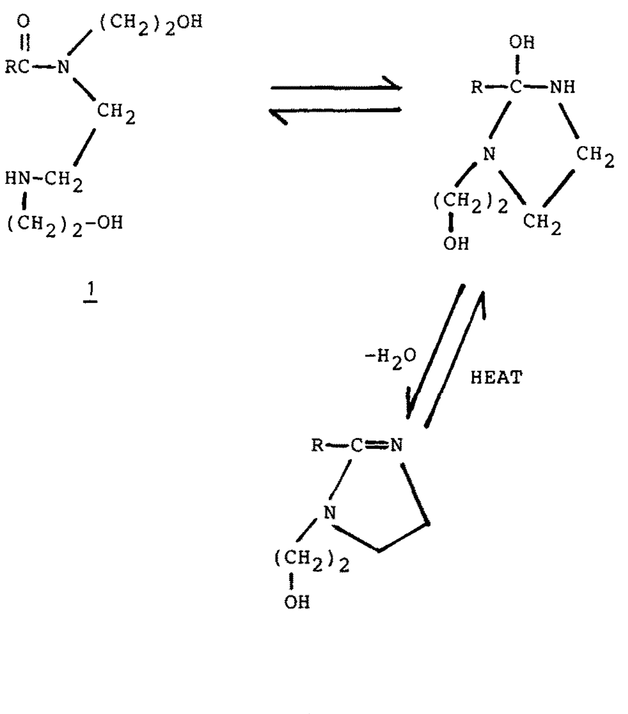

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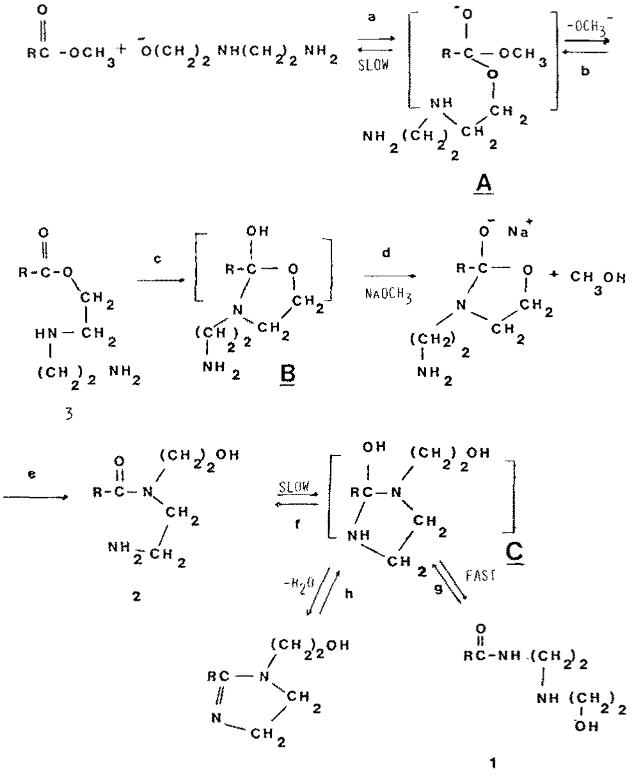

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Nonionic Surfactants in Municipal Sewage in Israel

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ABSTRACT

Nonionic surfactants are a significant factor in the municipal sewages profile, which, in turn, affects the efficiency of sewage-treatment processes and determines the possibility of sewage-water reuse. Hard (nonbiodegradable), nonionic surfactants are the most commonly used nonionics in Israel, which probably has no parallel in other western industrial countries. In view of the increased share of nonionic surfactants at the expense of anionic surfactants, a worldwide trend, municipal sewages in Israel were expected to contain increasing amounts of nonionic surfactants, unless the ratio between the biodegradable and nonbiodegradable nonionics used was significantly changed. In vivo determinations of nonionic surfactants in representative municipal sewage systems in Israel, applying a modified SDA-cobalt thiocyanate (CTAS) procedure and calibration curves (prepared under in vitro conditions), established typical concentrations of nonionic surfactants in municipal sewage in the northern part of Israel to be in the range of 3-4 mg/L. Under the particular local situation, a calibration curve derived from a mixture of nonylphenol ethoxylates (NP_{8-14}), having a slope of 0.165 absorbance units/mg of nonionic, can be reliably used to determine the content of nonionic surfactant of municipal sewage effluents. A correction factor based on the extent of nonionic recovery should be applied to ensure accuracy. All of the results obtained agree with other relevant studies and worldwide trends. The concentration of nonionic surfactants in municipal sewage in Israel appears to be decreasing. The results of the study, selected aspects involved with the determination procedure under in vivo conditions and issues relevant to the problem of nonionic detergents in municipal sewage, are discussed. The contribution of the study toward the improvement of water quality, thus increasing its potential for reuse in Israel (and elsewhere), is emphasized.

INTRODUCTION

Synthetic detergents, of which a substantial portion are nonionic surfactants (1), constitute a significant factor in the municipal sewage profile (2-4) in developed and developing countries all over the world. This factor, in turn, determines the possibility of sewage-water reuse after appropriate purification and recovery processes (5).

In Israel, which is a model of efficient water use (6), the reuse of recycled and reclaimed water is probably the most effective response to the scarcity of water resources in the quantity and quality required on the one hand, and the overexploitation of existing resources on the other. The reuse and exploitation of treated municipal sewage is no exception. The types, quantities and properties of the detergents present in such effluents constitute a determining factor as far as their removal is concerned (7). However, the reuse of water on a large scale opens a Pandora's box with respect to the environmental consequences involved (8).

THE PROBLEM AND SCOPE

The resistance to biological degradation is characteristic for a substantial portion of the existing types of nonionic surfactants (9). In addition to causing serious foaming problems, they interfere with sewage treatment processes, as do other types of synthetic detergents (4). Thus, the nonbiodegradable, branched-chain alcohol and alkylphenol ethoxylates are responsible for the various aspects of short- and long-term environmental problems involved in their use, i.e., economic-technological, biological-ecological and aesthetic-psychological. Combining the above information with the assertion that complex energy and environmental issues will dominate the future growth and apportionment of the surfactant business (10) enables one to appreciate both the scope and impact of the issue of nonionic surfactants in municipal sewage.

Indeed, surfactants are, at present, a £7.1 billion market with a growth rate of 2.7% a year in the US and Canada alone (11). Nonionic surfactants, which account for ca. 30% of the total production (12), are made up of ca. 200 commercially produced nonionics, of which alkoxylated linear alcohols not only make up the largest portion of this type (13), but also represent the fastest growing nonionic surfactant class.

The passage of governmental legislation in the western industrial countries, with respect to environmental constraints, has made criteria for large-volume surfactants such as alcohol ethoxylates (AE), in which the alkyl group is predominately linear, and alkylphenol ethoxylates (APE), in which the alkyl group, in most cases, is highly branched, more stringent than the foaming reduction required of the alkybenzenes sulfonates in the 1960's. Consequently, much research has been carried out, both in industry and academia, to assess the biodegradability and environmental safety of AE and APE. On the other hand, the global energy crisis stimulated the use of lower temperature, effective, soluble liquid detergents which, in turn, favor the more soluble and hardness-insensitive nonionic surfactants. As a result, we are now witnessing a significant shift in the relative share of nonionic detergents in the detergent market, at the expense of the so far dominant linear anionic detergents.

As a consequence of the above trends, municipal sewage is expected to contain increasing concentrations of nonionics surfactants, unless the ratio between the biodegradable and nonbiodegradable nonionics used is changed significantly in favor of the former. In reality, this means more ethoxylated linear alcohols (AE) at the expense of alkylphenol ethoxylates (APE).

Unfortunately, in Israel, where all the ethoxylated-based nonionic surfactants are imported from the US and Europe, the nonbiodegradable APE dominate the nonionic market. The growth of the consumption of nonionic surfactants in Israel (first introduced in the country in 1964) is shown in Table I.

The most commonly used APE in Israel are the branched-