Synthesis and Performance of Ester Quaternary Biodegradable Softeners

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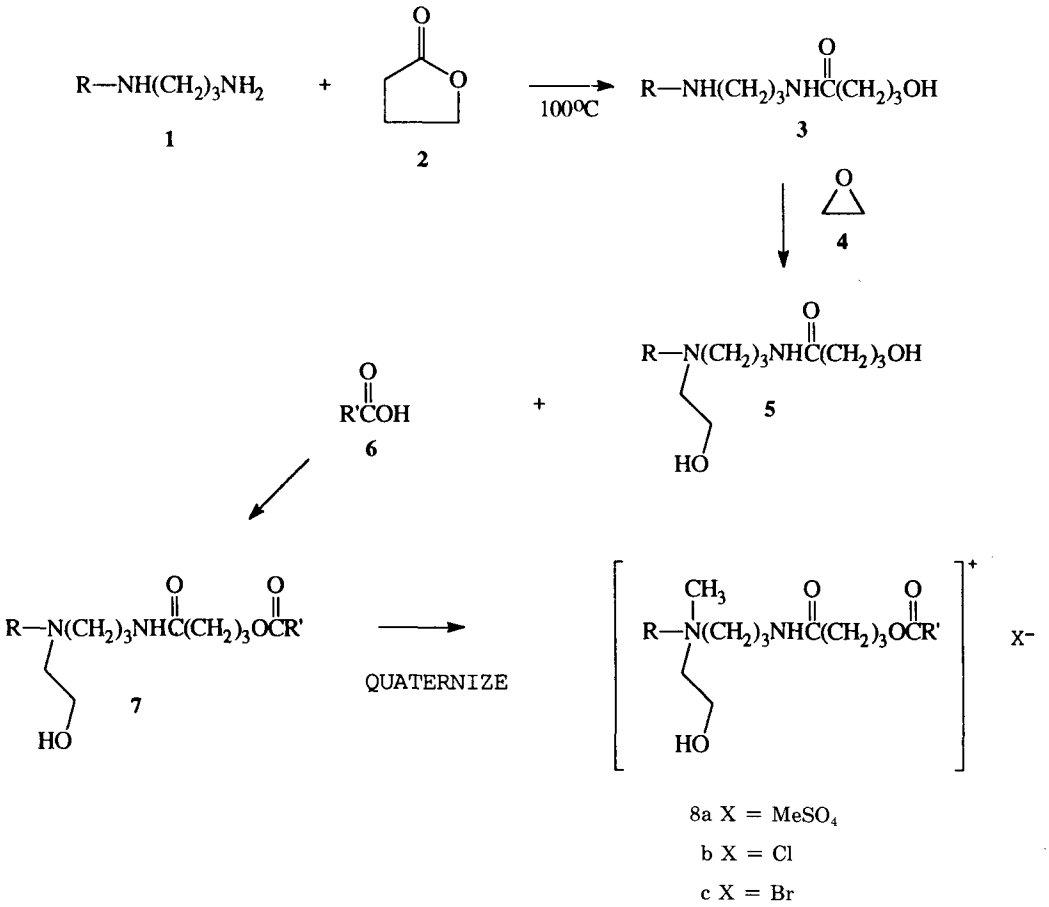
Reaction of hydroxyethylpiperazine with two moles of fatty acid, followed by quaternization with methyl chloride, methyl bromide or dimethyl sulfate, resulted in new quaternaries useful as biodegradable fabric softeners. Additional softeners were synthesized from hard tallow propane diamine by reaction with butyrolactone, followed by ethoxylation, esterification with one mole of fatty acid and quaternization.

KEY WORDS: Biodegradable, butyrolactone, ester quats, fabric softeners, hydroxyethyl piperazine, quaternaries.

Many commercial fabric conditioner formulations are based on quaternary ammonium salts, for example, dihydrogenated tallow dimethyl ammonium chloride (DHTDMAC). Within recent years, there has developed a need for fabric softening compositions with faster biodegradation, preferably two or three times faster than DHTDMAC. Quaternary compounds with long-chain alkyl groups interrupted by ester groups are known, and some attain rapid biodegradation (1-4).

Recent work (5,6) examined compositions containing quaternary ammonium salts that biodegrade rapidly but are sufficiently shelf-stable for commercial utility and provide satisfactory softening. Two structural types were prepared (see Schemes 1 and 2): (i) derived from butyrolactone [2] and (ii) derived from hydroxyethyl piperazine [9]. The reaction of amines with lactones is well known (7), and the resulting product is an amide-alcohol. It is also in the literature (8) that reaction of a polyamine with a lactone under controlled conditions will produce an amide-amino-alcohol, where reaction takes place exclusively at the primary amine function. The current series of biodegradable materials is based on that premise.

Reaction of a fatty diamine, such as tallow diamine [1], with a lactone, such as butyrolactone [2], results in an amine-amino-alcohol [3] that still has two reactive functional groups, the amine and the alcohol (Scheme 1). This material can be ethoxylated, and then esterified to



SCHEME 1

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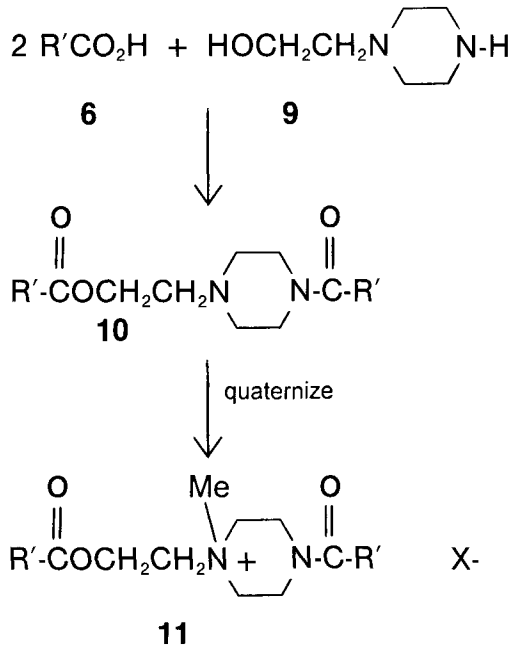

11a R' = myristyl, X = chloride
b R' = stearyl, X = chloride
c R' = hard tallow, X = methyl sulfate
d R' = oleyl, X = methyl sulfate
e R' = hard tallow, X = chloride
f R' = hard tallow, X = bromide

SCHEME 2

produce the amide–amino–ester [7], which is quaternized with various quaternizing agents to produce [8].

Reactions of hydroxyethylpiperazine are also known and have been controlled to selectively generate amides or esters (9–11). Here, two moles of fatty acid are used, and both an amide bond and an ester group are formed (Scheme 2). The remaining tertiary amine nitrogen is then quaternized to the final product [11].

EXPERIMENTAL PROCEDURES

Materials. Fatty acids, hard tallow diamine and DHTDMAC were standard products from Witco Corporation (Dublin, OH). Hydroxyethylpiperazine, butyrolactone and other reagents were obtained from Aldrich (Milwaukee, WI).

Methods. C-13 Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker WM200 FT NMR (Karlsruhe, Germany) and infrared (IR) spectra were done on a Mattson Galaxy Series 5000 Fourier transform IR (Madison, WI).

Biodegradation was conducted by a modified OECD301D method (12–15), which is a closed bottle test typically used for surfactants, where the consumption of oxygen is measured.

Fabric treatment, softening evaluation and static control were done according to procedures standardized by the Chemical Specialties Manufacturers Association (16–18). A 6% dispersion of the quats was formulated into a rinse cycle softener and used for these tests.

General procedure for the synthesis of adduct [3]. Into a 2-L four-necked flask was placed 800 g (2.46 moles) of hard tallow diamine [1]. The flask was fitted with a mechanical stirrer, reflux condenser, additional funnel and a thermometer. The amine was heated to 75°C, and 211.78 g (2.46 moles) of butyrolactone [2] was added at such a rate that the temperature was maintained between 100–110°C. After the addition was complete, the temperature was maintained at 100–110°C for 5 h. The total amine value (TAV) (19) was 143.8 (theor. = 138). C-13 NMR: 173.59 (C=O), 62.00 (CH_2OH), 50.00 (R-CH_2NH), 48.31 (R-CH_2NHCH_2), 38.90 (CH_2NCH=O), 34.01 (CH_2C=O), 31.96 ($CH_3CH_2CH_2$), 30.14 (R-CH_2CH_2NH), 29.73–28.47 (tallow methylene groups), 27.47 (CH_2CH_2OH), 27.01 (CH_2CH_2NHC=O), 22.71 (CH_3CH_2), 14.13 (CH_3).

General procedure for the synthesis of adduct [5]. Into a 2-L Parr reactor was charged 1300 g (3.20 moles) of [3], and the reactor was sealed and heated to 100°C. The reactor was then flushed with nitrogen. Then, 154.98 g (3.52 moles) ethylene oxide (EO; [4]) was added in increments by pressurizing the reactor to 50–60 psi with EO and allowing the pressure to drop to 20 psi as the EO was consumed. The EO addition was complete when the pressure stabilized at 50 psi. This took about 8 h. The contents were stirred for an additional 3 h after which the TAV = 125.5 and the III° AV = 120.4 (theor. TAV = III° = 125). C-13 NMR: 173.79 (C=O), 61.77 (O=CCH$_2$CH$_2$$CH_2$OH), 59.74 (N$CH_2CH_2OH$), 55.99 (NCH$_2$$CH_2$OH), 54.30 (R-$CH_2$N), 52.64 (R-$CH_2NCH_2$), 39.68 ($CH_2$NHC=O), 33.53 ($CH_2$C=O), 31.94 ($CH_3CH_2CH_2$), 29.98–28.53 (tallow methylene groups), 27.59 (CH_2CH_2OH), 26.83 (CH_2CH_2NHC=O), 22.69 (CH_2CH_3), 14.10 (CH_3).

General procedure for the synthesis of adduct [7]. Into a 3-L four-necked flask was placed 900 g (2 moles) of [5] and 568 g (2 moles) stearic acid. The flask was fitted with a mechanical stirrer, nitrogen sparge tube, Dean Stark trap, reflux condenser and thermometer. The contents were heated to 160°C while stirring and sparging with nitrogen. After 8 h, the acid value (AV) (20) was 3.53. The contents were cooled to 100°C and removed from the flask. TAV = 78.3 (theor. = 78.4). IR: 3300 cm^{-1} (OH and NH stretch), 1770 cm^{-1} (C=O ester), 1730 cm^{-1} (C=O ester), 1650 cm^{-1} (C=O amide). The two carbonyl bands in the ester region may be due to the formation of two ester isomers, as there are two hydroxyls that can be esterified. The C-13 NMR spectrum did indicate that there was a mixture of ester isomers formed. No residual fatty acid was present because only the ester and amide carbonyl bands were indicated in the material. The remaining peaks were too complicated to identify which ester isomers were present.

Procedure for the synthesis of [8a]. Into a 1-L three-necked flask was placed 400 g (0.56 mole) of melted [7] and 156.88 g isopropanol (IPA). The flask was fitted with a stir bar, reflux condenser, addition funnel and thermometer. The contents were heated to 60°C while stirring, and 70.63 g (0.56 mole) dimethyl sulfate (DMS) were added dropwise *via* the addition funnel, creating an exotherm. After the addition was complete, the contents were allowed to return to 60°C and stirred for an additional hour. At this time, the TAV was 0.84, and the AV was 7.16. The reaction was stopped at this point, and the contents were removed from the flask. The C-13 NMR spectrum of this material showed that a monomethyl quat was formed. The

methyl sulfate anion was also visible. The rest of the spectrum peaks were too broad to identify the isomers in this product.

Procedure for the synthesis of [**8b**]. Into a 2-L Parr reactor was placed 400 g (0.56 mole) of melted [**7**] and 133 g IPA. The reactor was sealed and flushed twice with methyl chloride by pressurizing to 35 psi and venting to 0 psi. Then the reactor was pressurized to 50 psi with methyl chloride. At this time, the temperature was 30°C. The contents were heated to 100°C, at which time the pressure reached 190 psi. After 6 h at 100°C, the TAV was 2.0 and the AV was 9.29. The reactor was cooled to 70°C at this point and vented to 0 psi, and the contents were removed from the reactor.

Procedure for the synthesis of [**8c**]. Into a 2-L Parr reactor was placed 400 g (0.56 mole) of melted [**7**] and 133 g IPA. The reactor was sealed and flushed twice with nitrogen by pressurizing to 50 psi and venting. Then the reactor was pressurized additionally with nitrogen to 50 psi and heated to 100°C, at which time the pressure rose to 78 psi. After one hour, the TAV was 1.26, and the AV was 4.97. At this point, the reactor contents were cooled to 70°C, vented and removed from the reactor.

Procedures for the synthesis of [**8d**] *and* [**8e**]. Identical to [**8a**], except hard tallow, fatty acids and soft tallow fatty acids, respectively, were substituted for stearic acid in preparation of adduct [**7**].

Procedure for synthesis of ester amide [**10**]. Two moles of the required acid [**6**] were placed in a 2-L four-necked flask. The flask was fitted with an additional funnel, air condenser, thermometer and mechanical stirrer. The flask was heated until the acid was melted, and then 1 mole (150 g) of 1-(2-hydroxyethyl)piperazine [**9**] was added dropwise *via* the addition funnel. After addition was complete, the flask was heated to 150–170°C, and the reaction was monitored by acid values. Periodically, the reaction was submitted to a water-aspirated vacuum to remove water from the system. A typical run usually took between 8 and 12 h. After completion of the reaction, the hot molten material was poured into two separate 1-L Erlenmeyer flasks and allowed to cool to room temperature.

After cooling, the material solidified. The solid material was dissolved in methylene chloride (or toluene), and $MgSO_4$ was added to the organic solution to remove any remaining water. The solution was filtered, and the organic solvent was removed *in vacuo*. The residual solid was recrystallized from ethyl acetate at 60°C.

Acid values ranged from 2–6 (theoretical 0.0). Total AVs ranged from 95–110 for the myristic acid derivative (theoret. 102) and 80–90 for the stearic acid derivative (theoret. 84.7). IR data showed two carbonyl bands at 1735 cm^{-1} (ester carbonyl) and 1655 cm^{-1} (amide carbonyl). No amine or hydroxyl bands were found. C-13 NMR confirmed the desired structure [**10**]. C^{13} NMR, 173.65 (amide carbonyl), 171.67 (ester carbonyl), 61.35 (CH_2OC), 56.71 (CH_2N), 53.21–53.52 (CH_2 ring N-CH_2), 45.61, 41.50 (CH_2 ring N-C), 34.35 (CH_2CO), 33.33 (CH_2CN), 29.20–31.99 (fatty chain), 25.44 (CH_2CH_2C-O), 25.04 (CH_2CH_2CN), 14.16 (CH_3).

Synthesis of methyl chloride quat [**11**]. The 318 g (0.578 mole) of the myristic acid ester amide of 1-(2-hydroxyethyl)piperazine [**10a**], 370 mL IPA and 64 g $NaHCO_3$ were placed in a 2-L Parr reactor. The reactor was sealed, and methyl chloride was charged into the reactor while stirring until the temperature and pressure stabilized (usually at 30°C and 50 psi). The reactor was heated to 100°C, and the reaction was monitored by TAV. Reaction times were normally between 6 and 8 h. After the reaction was complete, the reactor was cooled to 80°C and vented. The resulting mixture was vacuum-filtered, and the resulting filtrate was evaporated to dryness. Typical yields ranged from 95–100% for the myristic acid derivative [**11a**] and 91–93% for the stearic acid [**11b**] derivative. Free amine and amine hydrohalide analyses were 1.8, 1.8 and 2.3, 0%, respectively.

IR data showed two carbonyls present (1730 and 1645 cm^{-1}), ester and amide. C-13 NMR data showed a new peak at 48.56 (CH_3-N) and confirmed the structure. Chemical shifts of the other carbons were consistent with quaternary formation.

Preparation of methyl sulfate quat [**11c**]. One mole of [**10**] was weighed into a four-necked round-bottom flask. To that, enough IPA was added to make a 50%-solids solution. The flask was equipped with a mechanical stirrer, thermometer and condenser. DMS (0.95 mole) was added at 80°C *via* and additional funnel. When the DMS was all added, the reaction mixture was heated for one more hour.

RESULTS AND DISCUSSION

The basic concept behind the quat structures was that at least one ester group is needed to allow hydrolysis into smaller, more biodegradable molecular portions. It was thought that the presence of many functional groups would also facilitate chemical and biological breakdown. Both structures [**8**] and [**11**] contain amide groups, while [**11**] also has a hydroxyl function.

A number of structures were prepared based on fatty diamines and butyrolactone. An attractive feature of this series was that one fatty group could be changed independently of the other, giving unsymmetrical molecules and many possibilities to adjust the properties. Identical chemistry was done with caprolactone instead of butyrolactone, and similar products were obtained but not evaluated. Caprolactone is not as reactive as butyrolactone, and final products were not as pure.

Table 1 shows a comparison of the various performance criteria to the industry standard DHTDMAC. As can be seen, the performance changes dramatically with structure. The C-14 version of the piperazine structure [**11a**] biodegrades excellently, but softening is unacceptable.

TABLE 1

Performance[a]

Structure	Biodegradation	Softening	Formulation stability
DHTDMAC	19%	Excellent	Fair
11a	72	Poor	Good
b	47	Good	Fair
c	13	Good	Good
d		Poor	Excellent
e		Good	Poor
f	40	Good	Fair
8a	43	Excellent	Poor
b	14	Excellent	Good
c	21	Excellent	Fair
d	22	Excellent	Fair
e	33	Excellent	Excellent

[a]Percent of theory obtained in 20 d when tested at 1 ppm. DHTDMAC, dihydrogenated tallow dimethyl ammonium chloride.

Hard tallow and stearyl are best for softening, with the stearyl biodegrading somewhat better [**11b** *vs.* **11f** and **8a** *vs.* **8d**]. Previous work has shown that trialkyl quats soften better than dialkyls better than monoalkyls, that longer chainlengths are better than shorter, that saturated chains are better than unsaturated, and thus, in general, the higher the molecular weight, the better the softening. The butyrolactone structure [8] softens considerably better than [11], probably due to its higher molecular weight. This is one of the few structures to match DHTDMAC in softening.

Overall, [**8e**] (hard tallow–soft tallow) may be considered the best of the structures prepared because of its excellent softening and its ease of formulation, even up to 20% actives. Its biodegradation rate is much improved to DHTDMAC, but unfortunately, it is not as good as other structures. The most desirable goal is "ready biodegradability," which is greater than 60% degradation in 28 d (12).

REFERENCES

1. Naik, R.A., K.H. Todt and M.A. Wells, U.S. Patent 4,137,180 (1979).
2. Walley, D.R., European Patent Application 0,345,842 (1989).
3. Tandela, S.D., and B.W. Topping, European Patent Application 0,409,502 (1990).
4. Bauman, R.A., and J.A. Kaeser, U.S. Patent 4,339,391 (1978).
5. Friedli, F.E., and M.M. Watts, U.S. Patent 5,128,473 (1992).
6. Lagerman, R.K., S.F. Clancy, D.A. Tanner, N.L. Johnston, B.I. Callian and F.E. Friedli, *INFORM 3*:528 (1992).
7. Buc, S.R., and E.P. Williams, U.S. Patent 2,945,863 (1960).
8. Diehl, F.L., U.S. Patent 3,322,675 (1967).
9. Ernst, R., U.S. Patent 3,167,554 (1965).
10. Rato, H., T. Mouri and T. Nishikawa, U.S. Patent 4,068,069 (1978).
11. Rato, H., T. Mouri and T. Nishikawa, U.S. Patent 3,980,643 (1976).
12. The Organization for Economic Cooperation and Development (OECD), *Guidelines for Testing of Chemicals*, Paris, France, 1981, OECD Method 301 D.
13. Clancy, S.F., and D.A. Tanner, *Div. of Environ. Chem. Extended Abstr. 1991 31(1)*:117.
14. Clancy, S.F., and D.A. Tanner, *INFORM 2*:360 (1991).
15. Clancy, S.F., D.A. Tanner, M. Theis and H.H. Paradies, *Div. of Environ. Chem. Extended Abstr. 32(1)*:907, 1992.
16. *Chemical Specialty Manufacturer's Association, Detergents Division Test Methods Compendium*, 2nd edn., Washington, D.C., 1985, method for fabric treatment DCC-13A.
17. *Ibid.*, method for softener evaluation DCC-13B.
18. *Ibid.*, method for static control DCC-F.
19. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, edited by David Firestone, American Oil Chemists' Society, Champaign, 1990, Method Tf 2b-64.
20. *Ibid.*, Method Te 1a-64.

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