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SYNTHESIS OF NEW ZWITTERIONIC SURFACTANTS WITH IMPROVED SOLUBILITY IN WATER

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ABSTRACT: New neutral zwitterionic surfactants of the sulfobetaine series have been synthesized in a preparative scale in a two steps procedure. Ring opening of propane or butane sultone is obtained by a 2-methyl-1,3-cycloiminoether in a first stage, and the resulting inner cycloiminium sulfonate salt is ring-opened by a fatty tertiary amine. The introduction of an acetamide group between the two charged groups of the zwitterion enhances the solubility in water and then allows the use of octadecyl chained surfactants in water at room temperature. This synthesis provides pure compounds, free of inorganic ions, in good yield addition reactions from commercially available starting materials.

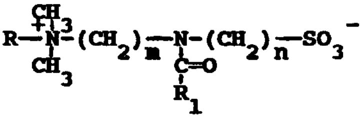
INTRODUCTION

Zwitterionic amphiphiles are compounds of growing interest because of their specific properties[1]. As their aqueous solutions, they are first poorly sensitive to ionic strength even to multivalent ions[2-4], contrasting with ionic amphiphiles. Second, they are weakly sensitive to temperature variations: the demixing on heating (clouding phenomenon) which occurs with nonionic amphiphiles has never been observed with zwitterionic ones. Many potential industrial applications have been recognized as dispersants, emulsifiers, foaming agents,...[1], the particular interest of zwitterionic surfactants in each application being related to their low sensitivity to external conditions (ionic strength, presence of multivalent cations, pH or temperature). Zwitterionic surfactants are moreover extensively used for biological purposes, as for non denaturing membrane proteins extraction[5-7], making of this class of compounds speciality materials.

Both tensioactive properties and solubilizing power of zwitterionic surfactants are limited by the solubility in water of long hydrophobic chained surfactants. Lengthening the alkyl chain, which should enhance these properties, results in an increase of the Krafft temperature (below which the surfactant is water insoluble)[8] above room temperature. In practice, the length of hydrophobic chains is currently limited to a maximum of 16 carbon atoms, as with most other types of surfactants.

In order to overcome this problem, hydrophilic groups are incorporated in the tensioactive molecules. Tensioactive zwitterionic compounds bearing hydrophilic groups such as hydroxyl[2,9], amide[10,11], sulfonamide[12] have been synthesized through various ways involving the use of commercially available materials. Among them, reagents of the imidazoline series are powerful for the preparation of hydrophilic zwitterionic compounds, but the reaction schemes generally used are not selective and lead to the formation of surfactants as mixtures which cannot be purified[13,14].

This paper deals with the synthesis of new zwitterionic surfactants with a polar group intercalated between the two electrical charges of the zwitterionic part of the molecule. The use of heterocyclic 1,3-iminoethers allows the introduction of a hydrophilic amide group between the two ionic groups of the zwitterionic part of molecule. A good selectivity in the chemical reactions is also obtained. The incorporation of this polar group enhances the solubility in water and allows the use of octadecyl chained surfactants in water at room temperature. The general chemical formula of these amphiphilic compounds is:

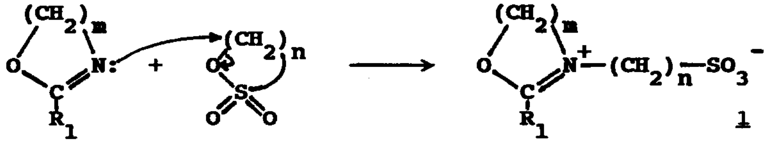


$$R-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-(CH_2)_m-\underset{\underset{R_1}{C=O}}{N}-(CH_2)_n-SO_3^-$$

where R is an alkyl chain which constitutes the hydrophobic part of the molecule, R_1 can in principle be varied at will as methyl, ethyl, phenyl,..., but only methyl substituted derivatives have been satisfactorily obtained, m = 2 or 3 and n = 3 or 4. The choice of m and n is limited because of the ring opening synthesis path.

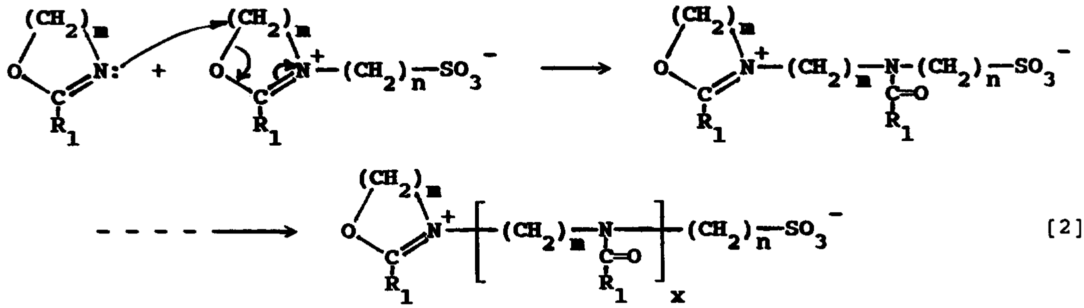
SYNTHESIS PROCEDURE

The synthesis involves two steps. Propane sultone (n = 3) or butane sultone (n = 4) is first ring opened by a simple addition of a 1,3-cycloiminoether as[15]:



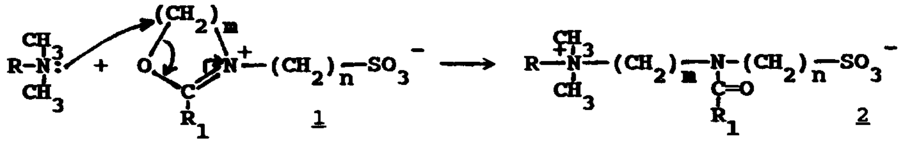
[1]

The nucleophilic attack of the imino group nitrogen occurs at the carbon 3 (or 4) of propane (or butane) sultone. A further reaction may then occur which is a nucleophilic ring opening of the cycloimminiumalkylsulfonate 1 at carbon 5 (or 6), which yields a polyalkyleneamide as[16-19]:


[2]

In certain cases, described in the following, this undesirable reaction is avoided by using stoechiometric amounts of sultone and 1,3-cycloiminoether, cycloimminiumalkylsulfonates 1 can be obtained without any detectable amount of polymerized material. It occurs when the first step [1] is faster than polymerization [2] and when polymerization is prevented by precipitation of 1 as and when it is formed. 1 is isolated from the reaction medium.

The second step is a ring opening of 1 by a tertiary amine through a nucleophilic attack at carbon 5 (or 6) as[15]:


[3]

This reaction yields the zwitterionic compound 2 in quantitative yield. The yield of recovered materials is however not quantitative because of incomplete precipitation. The possible attack at carbon 2 does not occur when it is sterically hindered[20,21] and with soft nucleophiles like tertiary amines[15]. Using an alkyldimethylamine bearing a fatty alkyl chain as a nucleophile, an amphiphilic compound is obtained with an amide group intercalated between the two charges.

The synthesis strategy in this two step procedure is based on the fact that 1,3-cycloiminoethers are nucleophiles at their nitrogen atom while cyclic oxaiminium salts (1) are electrophiles at their 5 methylene group (for 1,3-oxazolines, m = 2) or 6 methylene group (for (4H) 5,6-dihydro 1,3-oxazines, m = 3). The chemistry of these heterocycles has been recently reviewed[22,23]. The limiting reaction in this is the first step, in which no polymerization should occur. This has been studied as a function of the substituent at carbon 2 of the iminoether ring, with five or six membered cyclic iminoethers and propane or butane sultone as sulfonate source.

For the ring opening of the sultone to be fast as compared to polymerization, the cyclic iminoether has to be nucleophilic enough and the O-methylene (5 or 6) of the corresponding oxaiminium salt has to be of low electrophilicity. Three types of compounds (Table I) could be synthesized in this way although many other ones could be obtained with low yield and some supplementary practical difficulties. All these compounds were obtained with 2-methyl-1,3-cycloiminoethers but failure occurred with 2-methyl-1,3-oxazoline and butane sultone as polymerization competes with sultone ring opening. In this later case, the reaction is too slow at room temperature and heating is necessary for the reaction time to be reasonable. At 70°C, after complete conversion of the starting materials, the reaction yields a mixture of low molecular weight polymers with an average polymerization degree of 12. This behaviour is in agreement with the reactivity of these heterocycles. The six membered ring butane sultone is less reactive that the five membered ring propane sultone[24], and the nucleophilicity of 2-methyl-1,3-oxazoline is lower that 2-methyl-(4H)-5,6-dihydro-1,3-oxazine[19].

2-Ethyl- (or higher alkyl) and 2-phenyl-1,3-oxazolines could not be used successfully in the first step. 2-Ethyl-1,3-oxazoline and propane sultone in chlorobenzene yield the inner salt 1 as a precipitate with only 12% yield after one month reaction time at room temperature; heating at 50°C causes polymerization. In the same way, 2-phenyl-1,3-oxazoline and propane sultone react too slowly[15] and the inner salt 1 does not precipitate from chlorobenzene. The fact that no precipitation occurs is a major difficulty with a slow reaction as one has to ensure that the first reaction is quantitative before adding the tertiary amine. In the reaction medium, incomplete reaction leaves propane sultone, which is ring opened by the tertiary amine faster than the cyclic oxaiminium salt 1; a mixture of zwitterionic surfactants results for this incomplete conversion in the first step. As neither 2-ethyl-, nor 2-phenyl-1,3-cycloiminoethers can work for our purpose, the only 2-alkyl cyclic iminoether which can be used satisfactorily is the 2-methyl one and it is suspected that aromatic substituents should not work. Indeed, among the known 2-substituted cyclic iminoethers, 2-methyl ones are the most nucleophilic[19].

Following this procedure, surfactants given in Table I could be obtained from rather cheap reagents. 2-Methyloxazoline is an industrial compound[23]. As 1 precipitates from the reaction medium during the first step, separation of the salt 1 allows elimination of residual sultones which are known to be strongly carcinogenic. Octadecyl compounds can be recrystallized from acetonitrile, washed with acetone, and obtained very pure. Dodecyl compounds could not be recrystallized, they yield a viscous syrup after solvent evaporation and, although they analyse as pure compounds (elemental analysis, ^1H NMR, IR), may contain some traces of impurities, especially reaction solvent (dimethylformamide). The synthesis in one pot could in principle be

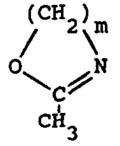
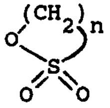
	REAGENTS				
Amine	1,3-cycloiminoether	Sultone	KRAFFT TEMPERATURE	CMC at 25°C	n°
$RN(CH_3)_2$					
R	m	n			
Dodecyl	2	3	< 0°C	-	2a
Dodecyl	3	3	< 0°C	-	2b
Dodecyl	3	4	< 0°C	-	2c
Octadecyl	2	3	14°C	$8.3\ 10^{-6}$ M	2d
Octadecyl	3	3	19°C	$7.1\ 10^{-6}$ M	2e
Octadecyl	3	4	22°C	$6.1\ 10^{-6}$ M	2f

Table I: Reagents used for the synthesis of zwitterionic surfactants and the surfactant Krafft temperatures.

possible as reactions are based on additions only, no by products being produced. However, the first step has to be a quantitative reaction, since unreacted sultone remaining in the reaction medium is easily ring opened by the tertiary amine in the second step. Actually, a complete conversion in the first step would require a very long time and a one pot synthesis is unrealistic. Satisfactory yields of the order 75-85% in the first step are obtained after a reaction time of 24 h.

SOLUBILITY IN WATER

The relevant quantity describing the ability to obtain aqueous solutions of surfactants is the Krafft temperature[8]. Above this temperature, the surfactant is soluble in water whatever its concentration. The complete schematic phase diagram of a water-surfactant binary mixture is shown in Figure 1. This peculiar behavior is due to the very large solubility of surfactant in water when micelles are formed. When the solubility is equal to the critical micellar concentration (cmc), excess surfactant which should precipitate remains in solution as micellar assemblies. The Krafft temperature is that temperature at which the solubility equals the critical micellar concentration. However, we report here Krafft boundary temperatures as measured in the region of the phase diagram where they do not depend on concentration (the vertical boundary in Fig 1), and call them (somewhat improperly) Krafft temperatures. This reported temperature is the important one for application purposes as the surfactant is water soluble at any concentration above it. The dodecyl chained surfactants which are presented here are water soluble at any temperature, their Krafft temperature is lower than 0°C. The Krafft temperature of octadecyl chained compounds are all in the room temperature region (Table I), which allows their practical use at moderate temperatures (20°C). For comparison, the Krafft temperature of N-octadecyl-N,N-dimethyl-3-ammoniopropylsulfonate is 73.4°C[25] and that of the ionic octadecyltrimethylammonium bromide is 39°C[26]. The low Krafft temperatures we have obtained are due to the incorporation of the polar acetamide group between the two charges of the zwitterion. The location of the polar group is very important for obtaining a low Krafft temperature. Indeed, the Krafft temperature of N-(3-heptadecylamidopropyl)-N,N-dimethyl-3-ammoniopropylsulfonate (synthesized according to ref 11) was measured as 107°C. This is a large difference although this compound ressembles closely those of this study, the location of its amide group outside of the zwitterionic moiety is thought to be the origin of such an effect. The surfactants of this study then seem more convenient for the use in aqueous solutions than this latter one which is a pure homologue of a commercial compound with mixed alkyl chains obtained from a fat cut[11]. It is difficult to provide a convincing explaination about the origin of these low Krafft temperatures without comparison with significant reference compounds. Such compounds are not available, however. The very high Krafft temperature of N-(3-heptadecylamidopropyl)-N,N-dimethyl-3-ammoniopropylsulfonate may be due to hydrogen bonding between amide N-H and C=O groups, providing a good stability to the crystalline state. Such an hydrogen is not available in our compounds. The problem of the origin of our low Krafft temperatures is still an open one. It may be the large separation between charged groups or the properties of the acetamide group. If properties of the acetamide group are concerned, this origin may be either its polarity, providing a favourable hydration energy in water, or its bulkiness which avoids crystallization. Cmc values at 25°C as obtained from surface tension measurements are given in Table I. Only those of octadecyl compounds could be obtained by this way since their purification by recrystallization is easy. Dodecyl compounds which do not crystallize are not pure enough for a correct surface tension measurement to be made. One should however not reject these compounds as impure ones because surface tension is very sensitive to impurities.

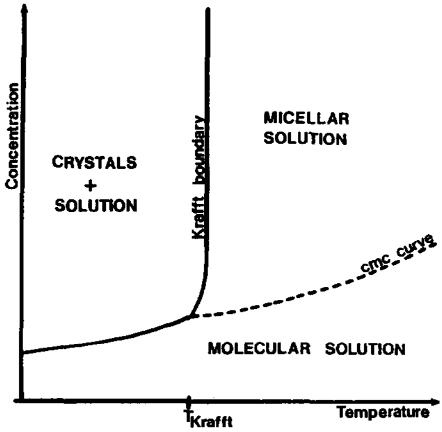


Figure 1: Schematic phase diagram of surfactant-water binary mixtures showing the Krafft boundary. The Krafft temperature is easily defined when the boundary is a vertical line in the diagram, which is actually observed with our compounds.

CONCLUSION

New zwitterionic surfactants of improved solubility in water have been synthesized. The introduction of an acetamide group between the two charged groups of the zwitterion allows the use of octadecyl chained surfactants in water at room temperature. The two steps synthesis procedure yields pure compounds in a good yield, upon addition reactions and thus, without production of any inorganic or volatile byproduct. Starting materials: fatty tertiary amines, 2-methyl cyclic iminoethers and sultones are moreover widespread commercial compounds. The potential application fields of such compounds can be wide, they have been tested for enhanced oil recovery[27] and are applied successfully to the emulsion polymerization of styrene, providing latexes of very narrow size distribution[28,29].

EXPERIMENTALS

^1H NMR spectra were run on solutions in CD_3OD with a continuous wave Bruker WP80 spectrometer (80 MHz) and with a Caméca TSN350 (350 MHz) for final compounds; chemical shifts are given in ppm from internal tetramethylsilane. IR spectra were run on KBr pellets with a Nicolet 20SX Fourier transform spectrometer, wave numbers are given in cm^{-1}. Elemental analyses were carried out at the Service Central d'Analyses of the CNRS (69390 Vernaison, France), theoretical elemental compositions (wt%) given in parentheses are calculated with some hydration water molecules named x in the following table. Melting points could not be determined since all these surfactants decompose before melting. All starting materials were distilled prior to use and solvents were dried on alumina and stored on 3Å molecular sieves. Krafft boundaries were determined by direct observation: a cold solution, initially below the Krafft boundary, was heated in a bath untill no remaining crystal could be observed with the naked eye. Samples were kept 1 hour for equilibration between each 0.5°C temperature step; 0.5°C is then taken as the uncertainty.

Oxaiminiumpropylsulfonate salts (1,n=3): stoechiometric amounts (1 mol) of propanesultone and 2-methyliminoether (2-methyl-1,3-oxazoline or 2-methyl-(4H)-5,6-dihydro-1,3-oxazine) were stirred in 500 ml of dry chlorobenzene for 24 h at room temperature under dry nitrogen. A precipitate of 1 appeared, precipitation was completed by addition of dry cyclohexane, 1 was then filtered under nitrogen, washed with cyclohexane and dried under vacuo. Compounds 1 were obtained as white hygroscopic crystals with 75 to 85% yields.

- m = 2, n = 3: IR: SO_3^- : 1035,1180; $C=N^+$: 1668

NMR: 2.17 (quint(J=7.0 Hz),2H); 2.48 (s,3H); 2.90 (t(J=6.5 Hz),2H); 3.90 (t(J=7.2 Hz),2H); 4.20 (t(J=10 Hz),2H); 4.95 (t(J=10 Hz),2H)

- m = 3, n = 3: IR: SO_3^- : 1040,1180; $C=N^+$: 1670

NMR: 2.3 (quint(J=6.0 Hz),2H and m,2H); 2.5 (s,3H); 2.88 (t(J=6.5 Hz),2H); 3.72 (t(J=6.0 Hz),2H); 3.88 (t(J=8.0 Hz),2H); 4.6 (t(J=5.5 Hz),2H)

Oxaiminiumbutylsulfonate salts (1,n=4): experimental procedures with butanesultone and 2-methyl-(4H)-5,6-dihydro-1,3-oxazine were the same as in the preceeding section but reaction temperature was 80°C (75% yield).

IR: SO_3^- : 1035,1190; $C=N^+$: 1655

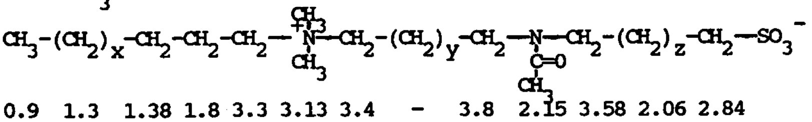
NMR: 1.7-2.0 (m,2H); 2.0-2.45 (m,4H); 2.5 (s,3H); 2.85 (t(J=6.5 Hz),2H); 3.25-3.7 (m,2H); 3.7 (t(J=6.0 Hz),2H); 4.6 (t(J=5.5 Hz),2H)

Tensioactive compounds of Table I: stoechiometric amounts (1 mol) of 1 and tertiary amine (dimethyldodecylamine or dimethyloctadecylamine) were heated for 3 h at 120°C in 500 ml of dry dimethylformamide under dry nitrogen. After cooling to room temperature, octadecyl compounds precipitated as white crystals, a more abundant precipitation was obtained upon addition of 500 ml of acetone, crystals were filtered, washed with acetone and dried under vacuo. The reaction was quantitative; the yield of recovered materials (after filtration and washing) was 70%. A further recrystallization is possible in acetonitrile. With dodecyl compounds, no crystallization was observed upon cooling the reaction mixture and a viscous syrup which could not be crystallized was obtained after evaporation of the solvent. For purifiation, the oily compound was dissolved in water (1 l) and washed three times with ether. Water was evaporated under vacuo and further drying was obtained by dissolving in dry methanol followed by evaporation. A vitreous compound resulted (90% yield), the powder obtained after grinding is very hygroscopic and is stored in a dessicator under nitrogen.

IR for all compounds: SO_3^- : 1040-1185; $\overset{+}{N}$-C: 1487; N-C=O: 1634

NMR:

compound (x,y,z)



$$CH_3-(CH_2)_x-CH_2-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_2-(CH_2)_y-CH_2-\underset{\underset{CH_3}{C=O}}{N}-CH_2-(CH_2)_z-CH_2-SO_3^-$$

compound (x,y,z)	CH_3	$(CH_2)_x$	CH_2	CH_2	CH_2	$N(CH_3)_2$	CH_2	$(CH_2)_y$	CH_2	$COCH_3$	CH_2	$(CH_2)_z$	$CH_2SO_3^-$
2a(8,0,1)	0.9	1.3	1.38	1.8	3.3	3.13	3.4	-	3.8	2.15	3.58	2.06	2.84
2b(8,1,1)	0.9	1.3	1.38	1.8	3.3	3.06	3.3	2.06	3.42	2.14	3.55	2.06	2.83
2c(8,1,2)	0.9	1.3	1.38	1.8	3.3	3.06	3.3	2.05	3.36	2.13	3.36	1.8	2.85
2d(14,0,1)	0.9	1.3	1.38	1.8	3.3	3.13	3.4	-	3.7	2.15	3.58	2.06	2.84
2e(14,1,1)	0.9	1.3	1.38	1.8	3.3	3.06	3.3	2.06	3.42	2.14	3.56	2.06	2.84
2f(14,1,2)	0.9	1.3	1.38	1.8	3.3	3.06	3.3	2.05	3.36	2.13	3.38	1.8	2.84
	t	m	m	m	m	s	m	m	t	s	t	quint	t
J(Hz)	6.3-6.7								6.9-7.7		7.7	7.2-7.5	7.0-7.1

Elemental analysis (wt%):

compound	2a	2b	2c	2d	2e	2f
x(H_2O)	0.6	3.0	2.0	0.0	1.0	0.2
C	58.7(58.46)	54.1(54.07)	57.0(57.00)	64.1(64.24)	62.3(62.64)	64.9(64.93)
H	10.7(10.56)	10.7(10.73)	10.9(10.81)	11.4(11.18)	11.3(11.26)	11.4(11.35)
N	6.4(6.49)	5.7(5.73)	5.8(5.78)	5.5(5.55)	5.1(5.21)	5.2(5.22)
O	17.1(17.06)	23.1(22.92)	19.6(19.80)	13.5(12.68)	15.1(14.90)	12.4(12.52)
S	8.0(7.43)	6.8(6.56)	6.9(6.61)	6.2(6.25)	6.2(5.98)	6.0(5.98)

Reaction of 2-methyl-1,3-oxazoline with butanesultone: Stoechiometric amounts (0.5 mol) of these compounds in 250 ml of chlorobenzene did not react at room temperature (or too slowly). At 70°C, complete conversion of iminoether was achieved after 70h. After cooling, precipitation of a waxy material occured and butanesultone was remaining in the solution. The precipitate was hydrolysed with water, washed with hot acetone and dried under vacuo, it analyses as a polymer of oxazoline with a number average polymerization degree of 12 (^{1}H NMR). It contained a butyl sulfonate group at one end and a 2-acetoxyethylammonio group at the other end resulting from the hydrolysis of the terminal cycloimminium group by water[15].

IR: SO$_3^-$: 1035,1170; $^+$N-C: 1478; N-C=O: 1640; O-C=O: 1743

NMR: 1.6-1.9 (m,4H); 2.13 (s,36H); 2.75-3.0 (m,2H); 3.0-4.0 (m,48H); 4.15-4.6 (m,2H)

Reactions of 2-ethyl-1,3-oxazoline and 2-phenyl-1,3-oxazoline with propanesultone: At room temperature, a stoechiometric mixture of 2-ethyl-1,3-oxazoline and propanesultone in chlorobenzene gave the 3-oxaiminiumpropylsulfonate salt 1 as a precipitate in low yield (12% after one month reaction time). With 2-phenyl-1,3-oxazoline a slow reaction occured (as checked by ^{1}H NMR analysis of a fraction) but the salt 1 does not precipitate, which made it difficult to obtain as a pure compound. Analysis of the reaction mixture with time have shown that considerable amounts of both starting materials were always present.

When 2-ethyl-1,3-oxazoline and propanesultone were heated at 50°C, precipitation of a waxy material occured and complete conversion of the starting cyclic iminoether was achieved after 24h. Analysis showed that polymerization had occured. The same occured with 2-phenyl-1,3-oxazoline; when dimethyloctadecylamine in dimethylformamide was then added to the precipitate free solution (3h at 120°C), a mixture of different compounds was obtained. N-octadecyl-N,N-dimethyl-3-ammoniopropylsulfonate precipitated first from the reaction mixture on cooling which was evidenced by its elemental analysis and ^{1}H NMR spectrum as compared to that of the pure compound synthesized by a method of the literature[30] (55% yield). The rest of the mixture obtained by evaporation of the solution and purification analysed as N-octadecyl-N,N-dimethylammoniopoly(ethylbenzamido)propylsulfonate with a number average polymerization degree of 2 to 3.

IR: SO$_3^-$: 1030,1190; $^+$N-C: 1496; phenyl: 1580,1600; N-C=O: 1630

NMR: 0.9 (t,3H); 1.0-1.35 (m,30H); 1.5-2.2 (m,4H); 2.5-4.25 (m,21H); 7.0-7.5 (m,7.5H)

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