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Professor Rainer Glaser, Associate Editor
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April 24, 2012

RE: **Revised**

Synthesis and Properties of N-(3-Oxapropanoxyl)dodecanamide: A Novel Surfactant for Use in Surfactant-Polymer Flooding

By Jessica Stokes and Charlotte Wesley

Dear Dr. Glaser:

Thank you for your response to our paper cited above. We appreciate and value the responses of the reviewers and changes have been made accordingly. The reviewers' comments and our replies are stated below.

Response to Reviewer 4:

[4.1] A leading reference and description of connate water were added.

[4.2] In regards to the figure legends, Figure 2 has a legend to help differentiate between the two plotted lines. Figures 1 and 2 show plots of only one line, which is described in the figure caption, making the inclusion of a figure legend redundant.

[4.3] Other uses have been mentioned in the conclusion.

[4.4] Both the ^{13}C - and ^1H -NMR spectra have been discussed thoroughly in the Supporting Information section.

Response to Reviewer 9:

[9.1] The word "head" was added after hydrophilic, as requested.

[9.2] The term "traditional well" was clarified using a more extensive sentence.

[9.3] We changed "decrease viscosity" to "decreased viscosity" as suggested.

[9.4] The sentence, "However, surfactants used in ASP flooding are usually in effective..." was clarified as to why it is referring to ASP flooding, and "in effective" was changed to "ineffective."

[9.5] A leading reference to and description of the term cloud point were added.

[9.6] On p. 10, “about” was changed to “approximately” in the sentence “The ideal concentration of the formulation...”

[9.7] Spacing has been adjusted per your request.

[9.8] Formatting of all references has been checked thoroughly to ensure consistent structure.

[9.9] Bibliography has been left with double-spaced format as it is intended to be part of the text and not formatted as endnote references.

[9.10] Discussion of a similar study using alkali flooding was added to compare the results of tertiary oil recovery.

Response to Reviewer 14:

[14.1] In regards to discussion of the NMR spectra see response [4.4].

[14.2] The actual name of the surfactant has been inserted to keep the paper flowing

[14.3] A page break has been added after the abstract as requested.

[14.4] Spacing has been adjusted per your request.

[14.5] Monotony was decreased by minor revisions to the paper.

[14.6] Grammar has been checked by means of detailed reviews by both authors.

[14.7] In regards to reference structure see response [9.8]

Other Minor Changes:

[0.1] Table formatting was updated to a more aesthetically pleasing design.

[0.2] Graphical abstracted was added.

[0.3] Additional sources were added to clarify tertiary recovery, ASP flooding, and SP flooding.

Once again, thank you for your consideration and reviews of our paper. We appreciate your time and advice. We hope that the revisions made will stand and allow for the publishing of our paper.

Sincerely,

Jessica Stokes and Charlotte Wesley

**Synthesis and Properties of *N*-(3-Oxapropanoxyl)dodecanamide: A
Novel Surfactant for Use in Surfactant-Polymer Flooding**

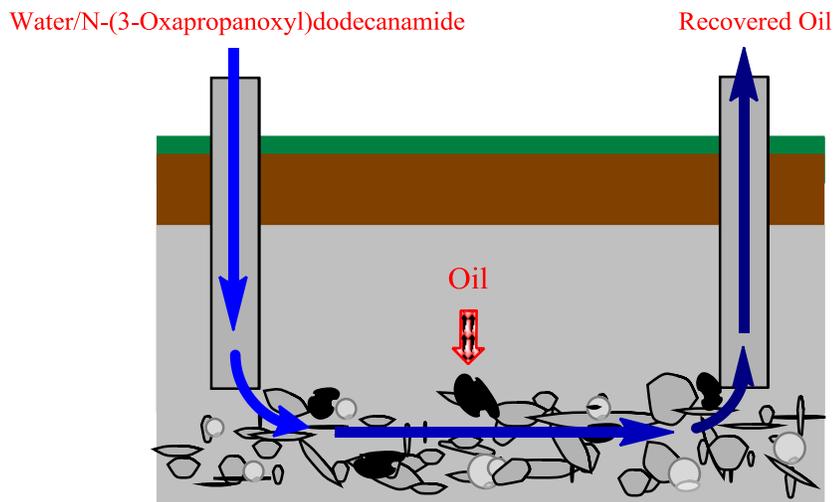
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Abstract

Surfactants are commonly used in the process of tertiary oil recovery with Alkali-surfactant-polymer (ASP) flooding as the most common method. However, recently the alkaline agent has brought about concern with environmental effects and productivity loss. A new recovery process, surfactant-polymer (SP) flooding, has been developed and surfactants that work without the alkali group need to be created. A novel surfactant, *N*-(3-Oxapropanoxyl)dodecanamide, has been synthesized and its surface activity properties have been tested. It is found that in combination with mixed micelles the surfactant has the ability to reduce the interfacial tension between oil and water to ultralow. In addition, oil recovery test show that, when used in conjunction with a polymer, *N*-(3-Oxapropanoxyl)dodecanamide has the ability to recover $18.6 \pm 0.4\%$ of tertiary oil reserves. These findings indicate that *N*-(3-Oxapropanoxyl)dodecanamide is ideal for use in SP flooding.



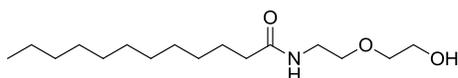
Surfactant-Polymer Flooding

Introduction

Surfactants are most commonly known for their use in soaps, detergents, and other cleaning agents. They have two main regions, a hydrophilic head and a hydrophobic tail, and can be classified into the three categories, anionic, cationic, and nonionic.¹ While surfactants are still best known for their cleaning purposes they have been found useful in other areas, such as oil recovery. In the collection of oil, there are three steps to its removal from the earth. The primary source of recovery is through a traditional well, which pumps out the flowing oil underground. Waterflooding is one method of secondary recovery, in which water is pumped into reservoirs to force out oil which has stopped flowing.² A common and useful tertiary oil recovery method is considered to be alkali-surfactant-polymer (ASP) flooding. In this process, the surfactant works to reduce the interface tension between the oil and water phases, while the alkali reacts with acids to create in situ surfactants and the polymer increases viscosity.^{3,4}

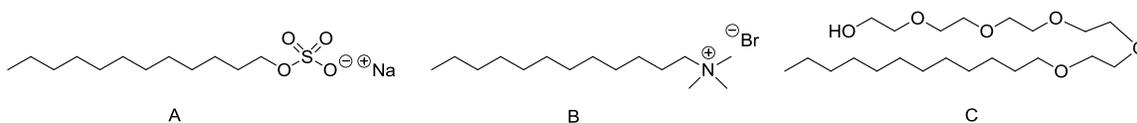
Although ASP flooding is considered useful, there are side effects due to the alkali.^{5,6} In the process of ASP flooding, most surfactants require a high concentration of alkali, which has contributed to multiple problems.⁶ It has caused erosion, reduced productivity, caused pumps to stick, and even decreased the viscosity of the polymers.^{6,7} These problems have led to the use of surfactant-polymer (SP) flooding, which does not use the alkaline agent. Surfactants used in ASP flooding are usually ineffective in SP flooding, due to the fact that the alkali group is no longer creating in situ surfactants.^{5,6} Therefore, new surfactants must be found and created for the use of SP flooding.

Here we report the results of the synthesis of the novel surfactant, *N*-(3-Oxapropanoxyl)dodecanamide (NOPD), and its application in surfactant-polymer flooding. NOPD was synthesized via the nucleophilic acyl substitution of lauroyl chloride with diglycolamide giving the structure shown in Scheme 1.



Scheme 1. Structure of *N*-(3-Oxapropanoxyl)dodecanamide

It is known alkanolamides are good surfactants for SP flooding because they do not show a cloud point; therefore, it is expected that as a dodecylmonoethanolamide derivative, NOPD would also be effective in SP flooding. A cloud point is the temperature or pressure at which the water solubility of a surfactant is reduced and a cloud solution results.⁸ This would be detrimental in SP flooding because the process of oil recovery relies on the formation of surfactant micelles in solution and the reduction of the surface tension of water. Additionally, since NOPD is nonionic we predict that—unlike cationic and anionic surfactants—it will not be absorbed into porous rock and will be effective even in the absence of alkali. In order to assess these hypotheses we tested the surface tension of a solution of NOPD in water and calculated the critical micelle concentration and the surface tension at that concentration. For comparison, we also tested the following common dodecyl surfactants: sodium dodecyl sulfate (SDS), dodecyl-trimethyl-ammonium bromide (DTAB), and dodecylpentaglycol (C₁₂E₅) (Scheme 2).

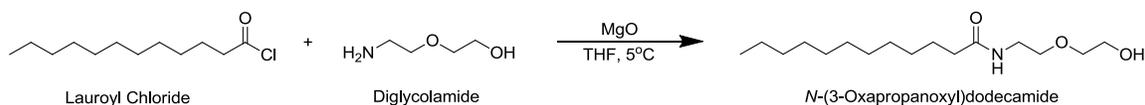


Scheme 2. A: SDS; B: DTAB; C: C₁₂E₅

In order to better understand the practical applications of NOPD in SP flooding, the tension between the between oil-water interface was measured and a technique was developed to measure the ability of a polymer-NOPD mixture to displace oil from an oil-saturated natural core.

Materials and Methods

The novel detergent, *N*-(3-Oxapropanoxyl)dodecanamide, is synthesized via the reaction of lauroyl chloride and diglycolamide in the presence of magnesium oxide. The solvent used is tetrahydrofuran and the mixture is allowed to react at low temperature for several hours (Scheme 3). For a more detailed description of the synthesis as well as spectroscopic characterization of the pure product see the accompanying appendix.



Scheme 3. Generalized Synthesis of NOPD

The usefulness of NOPD in regards to surfactant-polymer flooding is based on the surfactant's ability to form micelles. The critical micelle concentration (CMC) is simply

found as the concentration of surfactant above which micelles form and the molecule's effectiveness in reducing the surface tension of water is related to the surface tension of the solution measured at the CMC. This surface tension, γ_{CMC} , is measured using the du Noüy ring method. With this technique a platinum ring is suspended in solution and then the force required for the raised ring to break the surface of the liquid is measured.⁹

Using the Szyszkowski equation, $\Gamma = \frac{K}{1 + \frac{\gamma}{\gamma_{\text{CMC}}}}$, and the surface tension measurements the saturated adsorption (Γ^∞) and adsorption coefficient (K) can be calculated. Simple multiplication gives the cross section area of the air-water interface (a^∞) corresponding to each value of Γ^∞ . To better understand the relative effectiveness of NOPD, these tests were performed on additional, common surfactants with 12-carbon non-polar tails analogous to that of NOPD. The comparative surfactants used were the anionic surfactant SDS, cationic DTAB, and nonionic C₁₂E₅. The results of these measurements and calculations are shown in Table 1.

Surfactant	CMC (M)	γ_{CMC} (nM/m)	Γ^∞ (mol/cm ²)	a^∞ (nm ² /molec.)	K (M ⁻¹)
NOPD	1.5×10^{-4}	25.0	4.79×10^{-10}	0.35	2.21×10^{-5}
SDS	6.0×10^{-3}	36.6	3.18×10^{-10}	0.52	1.24×10^{-6}
DTAB	1.6×10^{-2}	38.7	3.20×10^{-10}	0.52	6.57×10^{-2}
C₁₂E₅	6.0×10^{-5}	30.4	3.20×10^{-10}	0.52	3.65×10^{-6}

Table 1. Surface Properties of NOPD and Three Comparable Detergents

In order to better understand the oil-water interface, the interfacial tension (IFT) between connate water and crude oil was measured using a Texas 500 model tensiometer.

Connate water is described as water that became trapped in rock at the time the sediment was deposited.¹⁰ The connate water solution we used consisted of 5 mM surfactants and 1000 mg/L of a partially hydrolyzed polyacrylamide (HPAM) polymer. The values were taken at 45°C and were measured over the course of about two hours until they no longer changed with time.

The practical effectiveness of NOPD in surfactant polymer flooding was tested by measuring the oil displacement from a naturally occurring core. The natural core was saturated with connate water and then saturated with oil to about 70%. Connate water was flushed through the core for the primary oil recovery. Following this a series of polymer, surfactant-polymer, and then polymer solutions were injected. The solution used consisted of *N*-(3-Oxapropanoxyl)dodecanamide at 0.3% weight and a polymer concentration of 1000 mg/L. The total oil recovery was measured and the difference between the total recovery and the primary recovery gave the tertiary oil recovery by surfactant-polymer flooding. A total of four natural cores were tested in this manner and the results are shown in Table 2.

Core No.	Core Permeability (10⁻³ μm)	Crude oil Saturation (%)	Recovery of Water Flooding (%)	Total Recovery (%)	Recovery of SP Flooding (%)
1	643	69.0	41.0	59.9	18.9
2	1258	67.5	38.7	57.2	18.5
3	1516	69.4	44.1	62.0	17.9
4	1542	76.6	41.0	60.0	19.0

Table 2. Results of Oil Displacement from Natural Cores

Results and Discussion

The results of the performance tests (Table 1) support the effectiveness of *N*-(3-Oxapropanoxy)dodecanamide as a surfactant. The concentration of NOPD required for micelle formation is much lower than that of SDS and DTAB, which indicates that the molecule is highly surface active. Likewise, NOPD has the lowest γ_{CMC} of the four detergents and can reduce the surface tension of water from 70 mN/m to 25 mN/m (Figure 1).

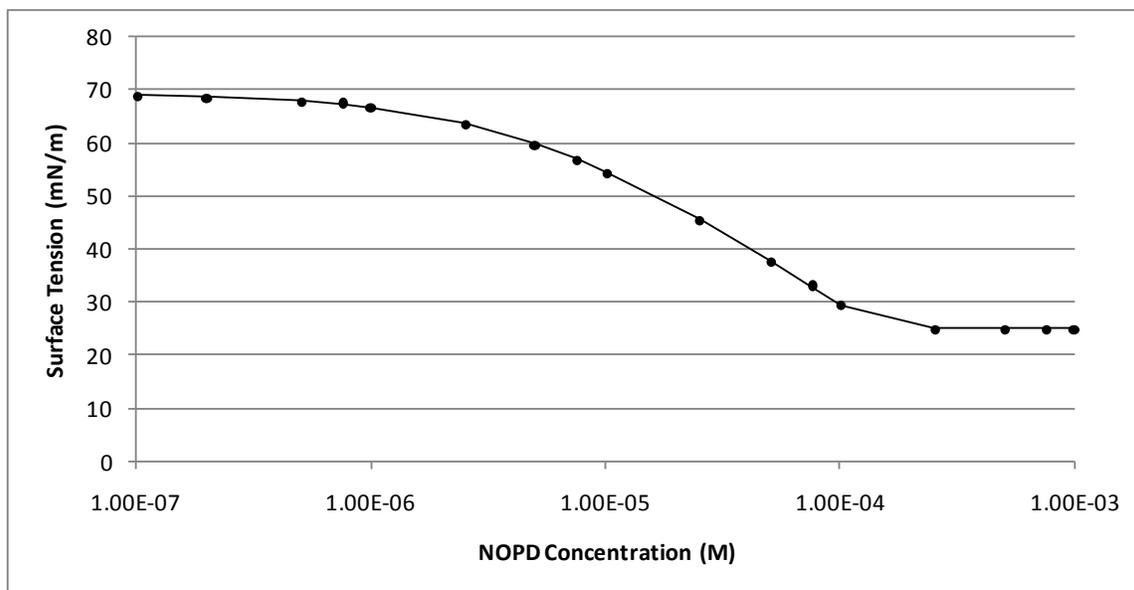


Figure 1. Surface Tension of NOPD at 45°C.

The saturated absorption of the tested surfactants were all relatively similar, however, the cross section area of NOPD was significantly smaller, indicating a more effective reduction of the IFT between crude oil and water.

From the measurements of interfacial tension it was found that the water solution of polymer and NOPD was not successful in decreasing the IFT to ultralow (mNm^{-1}) levels. However, this was to be expected because in general it is difficult for a single surfactant to decrease the IFT to ultralow. When NOPD was combined with a mixed betaine in a 0.45:0.55 mole-to-mole ratio, the ultralow IFT was reached without the addition of an alkaline agent. It should also be noted that the ultralow level was reached in only a few minutes and the IFT continued to decline over the course of two hours (Figure 2).

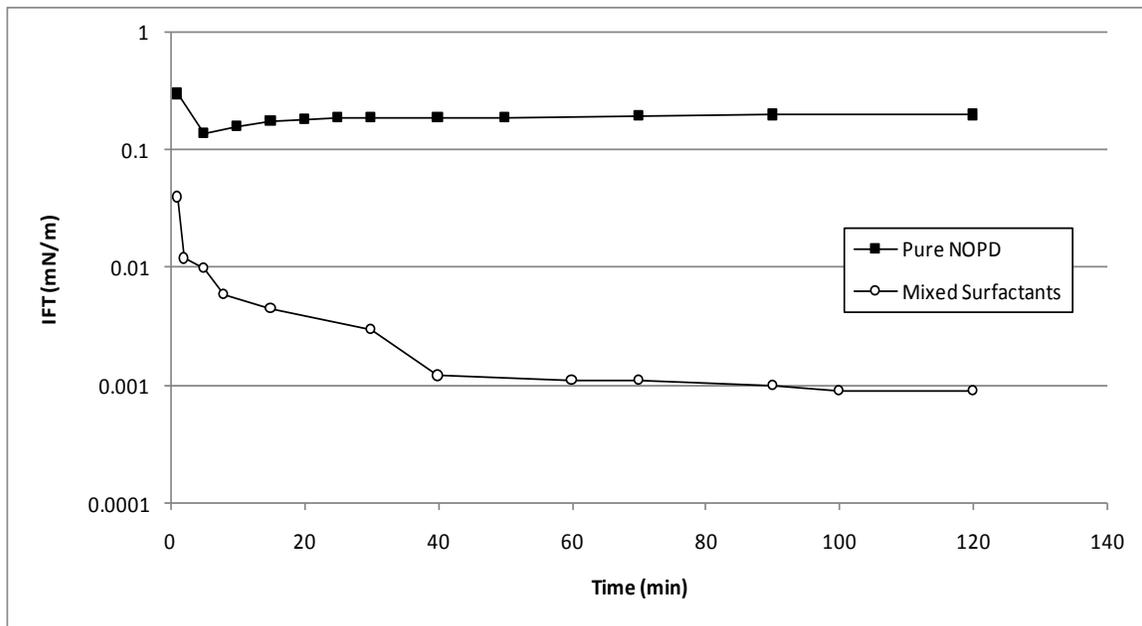


Figure 2. Dynamic IFT Between Crude Oil and Connate Water Solution at 45°C

Further IFT analysis of the polymer-mixed surfactants formulation showed that the ultralow level could be achieved over a wide range of concentrations. The ideal

concentration of the formulation is from approximately 0.1-0.2% weight; however, the equilibrium IFT is ultralow for concentrations from 0.01-0.5% weight. Figure 3 shows the equilibrium IFT for the mixed surfactants over this range of surfactant concentration.

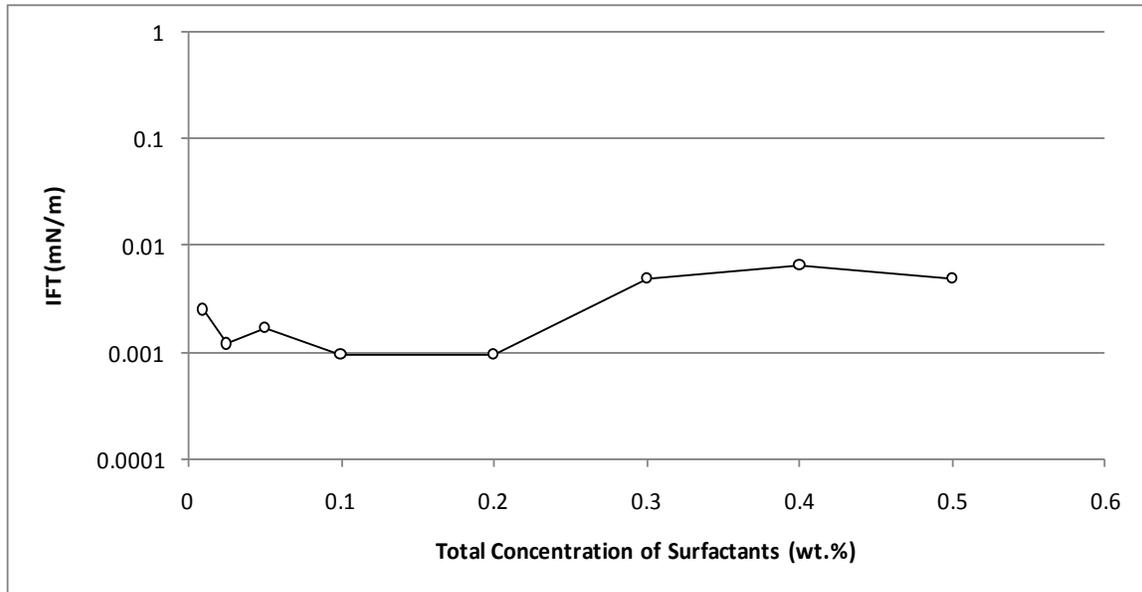


Figure 3. Equilibrium IFT Between Crude Oil and Connate Water with Different Concentrations of Mixed Surfactants

The data from the oil recovery process demonstrates the effectiveness of the NOPD-betaine mixture in SP flooding. On average these tertiary recovery methods resulted in an oil recovery of 18.6 ± 0.4 percent. In comparison to tertiary oil recovery methods we found that these results are on par if not slightly superior to enhanced oil recovery using alkali. Using a method similar to the one we employed, Samanta et al. reported that alkali flooding led to an average oil recovery of just over 14.5 percent.¹¹ In addition to the successful results of tertiary oil recovery, these experiments showed that,

as expected of a nonionic surfactant, NOPD does not have a cloud point. This allows NOPD to be used at high temperatures as well as in high salinity conditions.

Conclusion

N-(3-Oxapropanoxyl)dodecanamide was synthesized by the reaction of lauroyl chloride with diglycolamine and the product was confirmed to be pure by IR, ¹H-NMR, ¹³C-NMR, and ESI-MS. Surface tension measurements show a low critical micelle concentration and superior ability to reduce the surface tension of water when compared to common dodecyl surfactants, indicating high surface activity. The surface activity of NOPD is demonstrated by the surfactant's ability to reduce the interfacial tension between oil and water to ultralow levels when mixed with betaines. In oil displacement tests, tertiary recovery using the NOPD-betaine mixture averaged to 18.6%. This proves that *N*-(3-Oxapropanoxyl)dodecanamide is ideal as the main surfactant in surfactant-polymer flooding.

The use of *N*-(3-Oxapropanoxyl)dodecanamide poses a great potential benefit to the petroleum and oil industry. Alkali-free flooding also has fewer detrimental effects on the environment and drilling sites. Removing the alkaline agent would eliminate the erosion that occurs when it is introduced to a land formation. In addition, NOPD has the ability to reduce equipment malfunctions that are caused by the alkali group in ASP flooding. The alternative of using NOPD for SP flooding could eventually lead to saving money and time for the producers because cost of repairing drills or stabilizing the drilling locations would be minimized. Though no research has been done, there may

even be possibilities for NOPD to be used in oil recovery after spills or contamination of the environment. It is thus suggested that the integration of *N*-(3-Oxapropanoxyl)dodecanamide into tertiary oil recovery techniques could lead to advances in the oil recovery industry as well as other sectors of oil and petroleum industry.

Supplemental Material Available: The appendix contains information supplemental to the study of *N*-(3-Oxapropanoxyl)dodecanamide. This material includes a detailed description of the synthesis as well as spectroscopic characterization by mass spectrometry, infrared spectroscopy, and nuclear magnetic resonance.

References

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Supporting Information

Synthesis and Properties of *N*-(3-Oxapropanoxyl)dodecanamide: A Novel Surfactant for Use in Surfactant-Polymer Flooding

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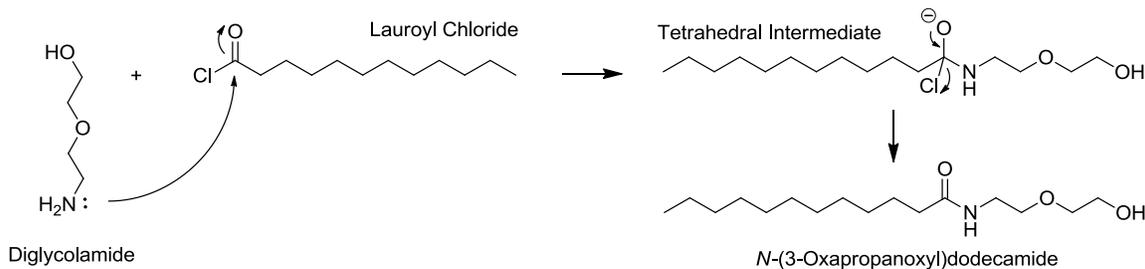
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Synthesis of *N*-(3-Oxapropanoxyl)dodecanamide

The *N*-(3-Oxapropanoxyl)dodecanamide was produced by reacting lauroyl chloride with diglycolamine (DGA) while magnesium oxide (MgO) was present. The exact synthesis consisted of the following: 4.41g (42mmol) of DGA was placed into a 250ml 3-neck flask. Then, 35ml of deionized water, 8.00g (200mmol) MgO, and 105mL of THF at 5°C was added to the flask. The mixture was allowed to stir for 30 min while cooling in an ice bath of 5°C. Next, a solution of 8.74g (40mmol) lauroyl chloride in 35mL THF was added dropwise over 1 hour with the use of a constant pressure funnel all while stirring at 5°C for a total of 2-2.5 hours. The MgO was then removed with filtration and the purified product was obtained by evaporating the filtrate in a vacuum to remove the THF. Pure water was then used to wash the product and it was dried at 50°C in a vacuum. This yielded a pure product in the form of a white powder. The mechanism for this synthesis is the nucleophilic acyl substitution of an acyl halide with a primary amine (Scheme S1).



Scheme S1. Mechanism for synthesis of *N*-(3-Oxapropanoxyl)dodecanamide

IR Spectrum of N-(3-Oxapropanoxyl)dodecanamide

Infrared analysis of NOPD (Figure S1) shows all the expected functional groups. The vibration stretch of C=O bond shows a peak at 1633.9 cm^{-1} . Just below this there is a peak at 1561.7 cm^{-1} that corresponds to the N–H bending. The wide peak at $3288.2\text{--}3400\text{ cm}^{-1}$ corresponds to the –OH stretch and the two peaks at 2916.1 cm^{-1} and 2847.6 cm^{-1} correspond to C–H stretches in the long alkyl chain.

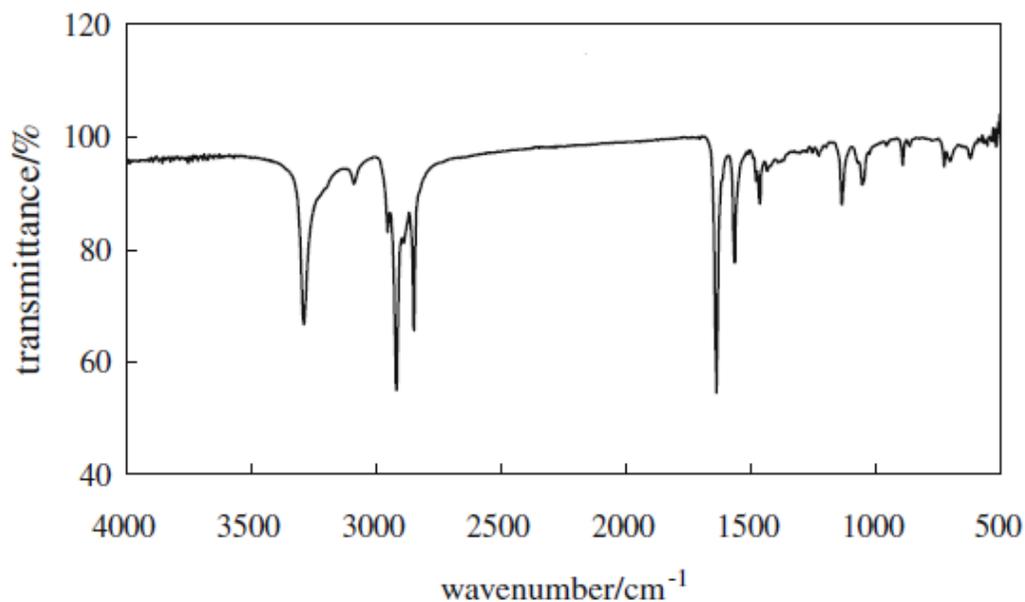


Figure S1. IR Spectrum of *N*-(3-Oxapropanoxyl)dodecanamide

ESI-MS spectra of *N*-(3-Oxapropanoxyl)dodecanamide

The ESI-MS spectrum of NOPD is shown in Figure S2. The mass of NOPD is 287.4; therefore, the peak at 288.3 m/z corresponds to the protonated molecule and the peaks at 311.2 m/z and 597.5 m/z correspond to $[M + Na^+]$ and $[2M + H^+]$ respectively. The lowest peak at 226.2 m/z represents the loss of the $-OCH_2CH_2OH$ fragment.

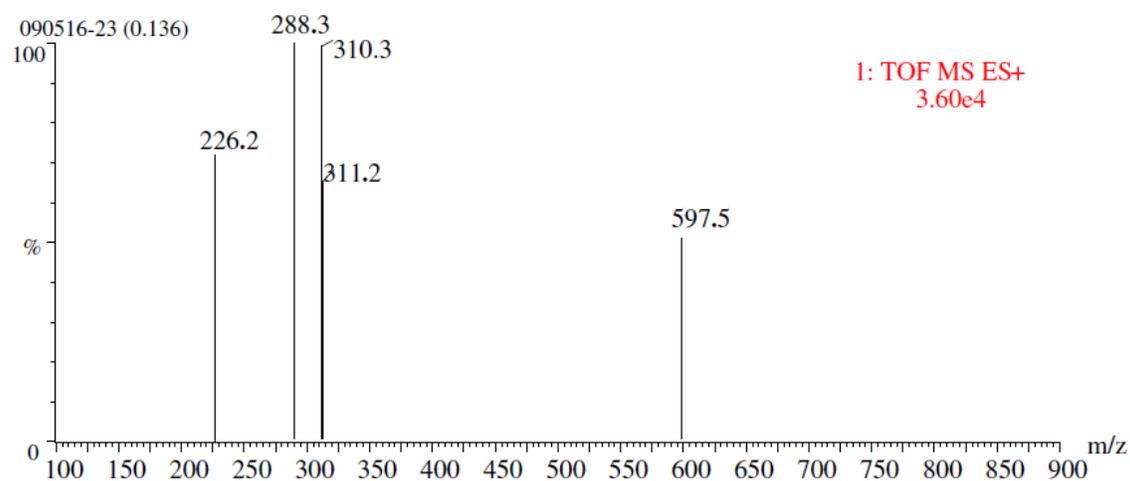


Figure S2. ESI-MS spectra of *N*-(3-Oxapropanoxyl)dodecanamide

Proton NMR Spectrum of *N*-(3-Oxapropanoxy)dodecanamidest

The structure of NOPD was further confirmed by NMR analysis. The ^1H -NMR is shown in Figure S3. The peak furthest to the left at about 8.0 ppm corresponds to the secondary amide hydrogen. The cluster of peaks between 3.0 ppm and 4.0 ppm account for the nine hydrogens in the head group of the molecule including eight methylene hydrogens and one alcohol. These hydrogens are all shifted downfield due to interactions with the amide, the ester, and the alcohol. The hydrogens in the tail group of the molecule correspond to the peaks between 0.5 ppm and 2.5 ppm, with the hydrogens alpha to the carbonyl having the highest shift and decreasing down the molecule.

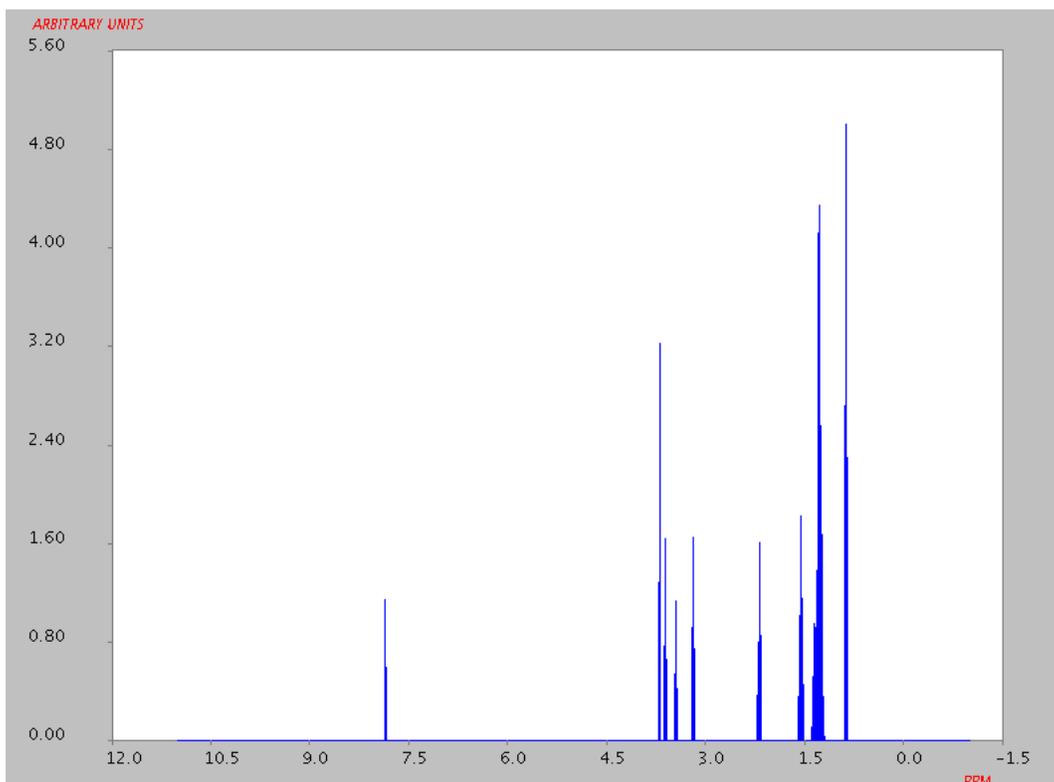


Figure S3. Proton NMR Spectrum of *N*-(3-Oxapropanoxy)dodecanamide at 400MHz

Carbon-13 NMR Spectrum of *N*-(3-Oxapropanoxyl)dodecanamide

The ^{13}C -NMR (Figure S4) is included as further evidence of the structure and purity. The peak at 172 ppm corresponds to the carbonyl carbon. Upfield from this the peaks at 70 and 72 ppm correspond to the two carbons alpha to the ether and the peak at 60 ppm correspond to the carbon alpha to the alcohol. These are shifted downfield from their expected positions due to the close proximity to electron withdrawing groups. The peak at 40 ppm corresponds to the other carbon in the head group that is alpha to the amide. The next peak at 37 ppm relates to the first carbon in the tail and the cluster of peaks from 30 - 14 ppm corresponds to the remaining 10 carbons in the tail group.

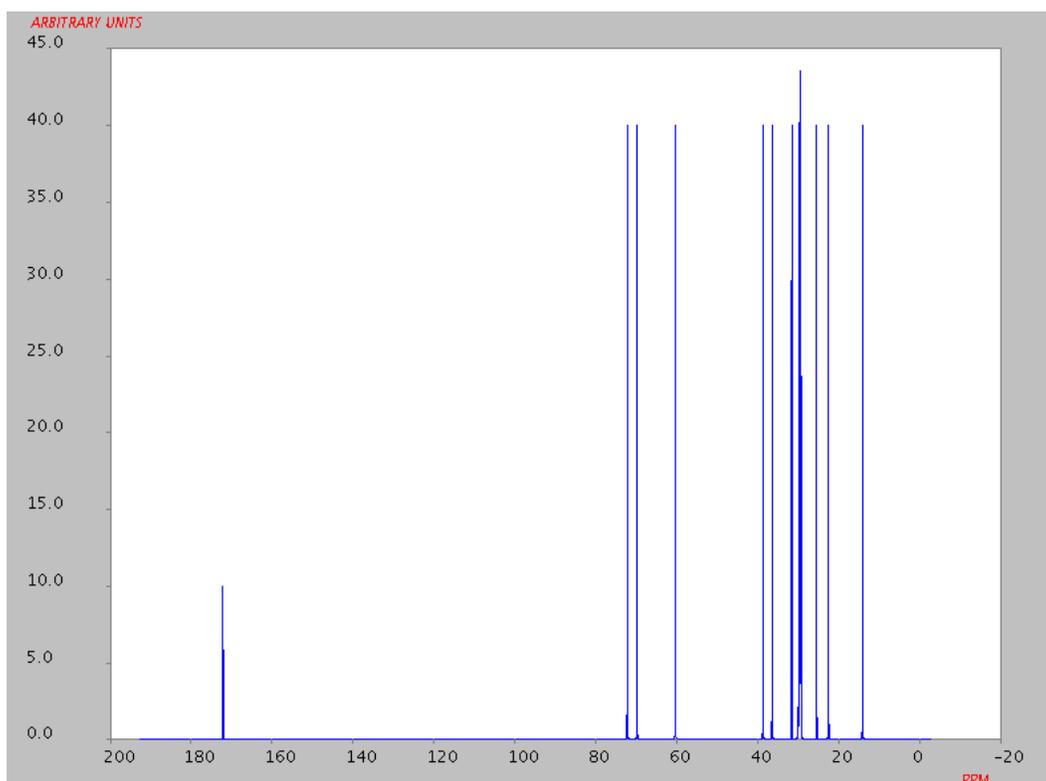


Figure S4. ^{13}C Carbon NMR Spectrum of *N*-(3-Oxapropanoxyl)dodecanamide in TMS

Bibliography

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