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## ORGANIC CHEMISTRY | SHORT COMMUNICATION

# A route to simple nonionic surfactants

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**Abstract:** A method for the synthesis of nonionic surfactants – *N*-alkyl-*O*-(2-hydroxyethyl) carbamates is proposed by acylation of fatty amines with ethylene carbonate without any solvent or catalyst. The surface tension of the prepared surfactants was measured, toxicity and biodegradability were determined for the surfactant with *n*-dodecyl as a hydrophobic group and *N*-monosubstituted amide and hydroxyl groups for their hydrophilic part.

**Subjects:** Chemistry; Materials Science; Physical Sciences

**Keywords:** surfactants; nonionic surfactants; synthesis; surface tension; toxicity; biodegradability

### 1. Introduction

Surfactants can be found among the most widely spread man-manufactured substances in the world, and they are produced in millions of tons per year. Very strict regulations are in place for their utilization/exploitation and production. They should not only be highly efficient in washing and cleaning processes but also practically nontoxic, sufficiently biodegradable, and reasonably cheap to make their application favorable to people. Various methods are elaborated for production of modern surfactants, both chemical and enzymatic (Friedli, 2001; Holmberg, 2003; Rosen & Kunjappu, 2013; Rosenholm, 2014; Somasundaran, 2006) allowing the preparation of anionic, cationic, zwitterionic, and nonionic surfactants, useful for different applications. Syntheses of these surfactants usually include several stages and demand time. Prices of reagents and the degree of complexity of their preparations together with the biological properties of these surfactants quite frequently limit exploitation of such surfactants. Therefore, the elaboration of a straightforward method for the synthesis of nonionic surfactants is discussed in this communication.

### 2. Results and discussion

Recently we have found that a simple acylation reaction of primary alkyl amines (**2**) with ethylene carbonate (**1**) at reasonably high temperatures (~150°C) resulted in the formation of promising non-ionic surfactants—*N*-alkyl carbamates with hydrophobic alkyl group at nitrogen atom and N-H and O-H bonds in the hydrophilic parts of the surfactants (**3**) (Scheme 1).

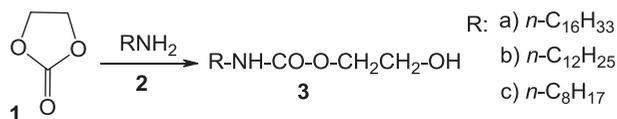
#### ABOUT THE AUTHORS

Sindija Brica, Maris Klavins, and Andris Zicmanis are interested in the development of modern surfactants with better biodegradability than existing ones useful for different applications. Their research is focused on the elaboration of such materials that might be produced in a large scale, including industrial production.

#### PUBLIC INTEREST STATEMENT

This paper describes a simple method for the preparation of nonionic surfactants that are useful in different exploitation areas. These surfactants form by heating fatty amines with ethylene carbonate at 150°C without any other solvent or catalyst. Obtained surfactants have surface activity comparable to other nonionic surfactants, and they are highly biodegradable materials. Therefore, they may be used when the simplicity of their preparation is important.

**Scheme 1. Reaction scheme showing the acylation reaction of primary amines with ethylene carbonate.**



Preparation of these surfactants is extremely simple—just heating both reagents **1** and **2** in equimolar ratio without any solvent, any catalyst and any inert gas protection. The simplicity of the proposed method differs it from approaches described in literature for similar purposes (Fujita, Bhanage, Kanamaru, & Arai, 2005; Hazard, Cheymol, Charbrier, Sekera, & Eche-Fialaire, 1961; Sekera, 1962). Acylation reactions of alcohols with freshly prepared carbamoyl chlorides (Hazard et al., 1961; Sekera, 1962) or transesterification reactions of corresponding carbamates with alcohols proposed by various authors (Fujita et al., 2005; Hazard et al., 1961) are very much more complicated and time-consuming methods for fabrication of carbamates. Even the recently shown acylation of octylamine with ethylene carbonate has required the use of a poisonous catalyst— $\text{Bu}_2\text{Sn}(\text{OCH}_3)_2$ , and the necessity to remove the excess of amine under vacuum at the end of the process (Hellawell et al., 2014). Traces of poisonous and dangerous catalyst have been acceptable in compositions of greases—the subject of a patent (Hellawell et al., 2014) but their presence is certainly not imaginable in materials foreseen for washing and cleaning.

Structures of obtained carbamates (**3**) were confirmed by their  $^1\text{H-NMR}$  and IR spectra; acceptable data of elemental analyses were also obtained. Good correspondence of spectral and analytical data was achieved (Table 1).

Sufficiently long linear carbon atom chains ( $\text{C}_8 - \text{C}_{16}$ ) form the lipophilic part of the proposed surfactants, and N–H bond of monosubstituted amide group together with O–H bond provide acceptable surface tension (32–43 mN/cm) and critical micelle concentration (cmc, 8.4–11.9 mg/L) for these novel surfactants (**3**) (Table 2). The surface tension of obtained *N*-alkyl carbamates (**3**) measured by the du Noüy ring method at 25°C differs a little depending on the length of alkyl chain but remains in range typical for nonionic surfactants (Friedli, 2001; Holmberg, 2003; Rosen & Kunjappu, 2013; Somasundaran, 2006).

**Table 1. Yields and analyses of surfactants–carbamates**

Surfactant	Yield, %	M.p., °C	Analyses, %*			$^1\text{H-NMR}$ spectra, $\delta$ , ppm**			IR spectra, $\text{cm}^{-1}$ ***		
			C	H	N	$\text{CH}_2\text{OC}$	$\text{CH}_2\text{OH}$	$\text{CH}_2\text{N}$	$\nu_{\text{C=O}}$	$\nu_{\text{N-H}}$	$\delta_{\text{N-H}}$
<b>3a</b>	79.8	78–80	$\frac{69.46}{69.25}$	$\frac{12.16}{11.93}$	$\frac{4.28}{4.25}$	4.20	3.80	3.17	1,685	3,353	1,541
<b>3b</b>	79.1	58–60	$\frac{66.01}{65.89}$	$\frac{11.60}{11.43}$	$\frac{5.14}{5.12}$	4.20	3.80	3.17	1,685	3,298	1,568
<b>3c</b>	79.0	45–46	$\frac{60.75}{60.80}$	$\frac{10.84}{10.67}$	$\frac{6.26}{6.45}$	4.19	3.79	3.16	1,699	3,311	1,551

\*Found results vs. calculated data.

\*\*Determined in  $\text{CDCl}_3$  solution on *Varian 400 NMR* spectrometer, internal standard TMS.

\*\*\*Registered in KBr tablet on the instrument *Perkin Elmer Spectrum One*.

**Table 2. The behavior of surfactants–carbamates in water solutions**

Surfactant	Surface tension, mN/cm*	cmc, mg/L
<b>3a</b>	42.1	11.9
<b>3b</b>	38.5	9.8
<b>3c</b>	32.5	8.4

\*Determined by the du Noüy ring method at 25°C at concentrations of surfactants 100 mg/L.

It should be mentioned that these surfactants are also comparatively nontoxic substances. *Daphnia*'s are the most commonly used crustacean test species for determination of the effects of xenobiotics on primary consumers in freshwater aquatic ecosystems (*Daphtoxkit F Magna*, 2000). EC<sub>50</sub> (half maximum effective concentration) for the carbamate **3b** after 24 and 48 h was found to be 2 and 0.5 mg L<sup>-1</sup>, respectively. The comparison of our results obtained for *Daphnia magna* with earlier literature in the context of ecotoxicity (EC<sub>50</sub>) of carbamates showed that surfactant **3b** displayed similar or lower toxicity than other surfactants (Rosen & Kunjappu, 2013; Somasundaran, 2006). Germination tests with *Lepidium sativum* L., *Raphanus sativus* L. and *Secale cereale* L. in the concentration range of the surfactant **3b** from 0.5 to 100 L<sup>-1</sup> did not reveal any inhibition effect.

The biodegradability of the surfactant **3b** was determined by CO<sub>2</sub> evolution in sealed vessels (*OECD Guidelines for the Testing of Chemicals*, 2014). BOD<sub>3</sub> test has revealed some difference between sets amended with surfactant **3b** (10 mg L<sup>-1</sup>) and control without any chemical. After 72 h incubation period, oxygen consumption and without it was found to be 18.4 ± 2 mg L<sup>-1</sup> and 8.4 ± 0.0 mg L<sup>-1</sup>, respectively. The results indicate potentially high biodegradability of the surfactant **3b** by microorganisms (Holmberg, 2003; Rosen & Kunjappu, 2013; Somasundaran, 2006).

### 3. Experimental

All reagents were used as purchased from commercial suppliers without further purification. All melting points were determined in open capillaries, using Thomas Hoover melting point apparatus, expressed in °C, and are uncorrected. <sup>1</sup>H-NMR spectra of the compounds were recorded on Varian 400 MR NMR spectrometer using TMS as an internal standard. Infrared spectra (IR) were recorded on Perkin Elmer Spectrum One Infrared Spectrometer, and samples were screened in potassium bromide (KBr) pellets. Elemental analyses were performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation).

**N-Dodecyl-O-(2-hydroxyethyl)-carbamate (3b)** (a typical experiment). Dodecyl amine (5.55 g; 30 mmol) and ethylene carbonate (2.64 g; 30 mmol) were stirred in a round bottom flask at 150°C (±5°C) for 3 h. No inert gas protection was required. *tert*-butyl methyl ether (40 mL) was added to the cooled to ~90°C reaction mixture, and the obtained solution was carefully mixed. The precipitate was separated from the mother liquid by suction using a Büchner funnel after keeping the reaction mixture at room temperature during 16 h. The precipitate was dried in open air. *N*-Dodecyl-O-(2-hydroxyethyl)-carbamate (**3b**, 6.48 g, 79.1%) was obtained in the form of white crystals with m.p. 58–60°C. Found, %: C, 66.01; H, 11.60; N, 5.14. C<sub>15</sub>H<sub>31</sub>NO<sub>3</sub>. Calculated, %: C 65.89; H, 11.43; N, 5.12. <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, δ-ppm): 4.78 (m, 1H); 4.20 (t, 2H); 3.80 (t, 2H); 3.18 (m, 2H); 2.42 (m, 1H); 1.49 (t, 2H); 1.27 (m, 18H); 0.88 (t, 3H). IR spectrum (KBr ν<sub>max</sub> cm<sup>-1</sup>): 3,298 (ν, N-H); 2,951–2,853 (ν, C-H); 1,685 (ν, C=O); 1,568 (δ, N-H).

Other carbamates (**3a** and **3c**) were prepared and characterized in a similar way.

**N-Hexadecyl-O-(2-hydroxyethyl)-carbamate (3a)**, yield 79.8%, white crystals, m.p. 78–80°C. Found, %: C, 69.46; H, 12.16; N, 4.28. C<sub>19</sub>H<sub>39</sub>NO<sub>3</sub>. Calculated, %: C 69.25; H, 11.93; N, 4.25. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, δ-ppm): 4.77 (m, 1H); 4.20 (t, 2H); 3.80 (t, 2H); 3.17 (m, 2H); 2.39 (m, 1H); 1.49 (t, 2H); 1.25 (m, 26H); 0.88 (t, 3H). IR spectrum (KBr ν<sub>max</sub> cm<sup>-1</sup>): 3,353 (ν, N-H); 2,951–2,853 (ν, C-H); 1,685 (ν, C=O); 1,541 (δ, N-H).

**N-Octyl-O-(2-hydroxyethyl)-carbamate (3c)**, yield 79.0%, white crystals, m.p. 45–46°C. Found, %: C, 60.75; H, 10.84; N, 6.26. C<sub>11</sub>H<sub>23</sub>NO<sub>3</sub>. Calculated, %: C 60.80; H, 10.67; N, 6.45. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, δ-ppm): 4.87 (m, 1H); 4.19 (t, 2H); 3.79 (t, 2H); 3.16 (m, 2H); 2.42 (m, 1H); 1.48 (t, 2H); 1.28 (m, 8H); 0.87 (t, 3H). IR spectrum (KBr ν<sub>max</sub> cm<sup>-1</sup>): 3,311 (ν, N-H); 2,951–2,853 (ν, C-H); 1,699 (ν, C=O); 1,551 (δ, N-H).

#### 4. Conclusion

Accordingly, our results confirm that primary fatty alkyl amines can be very easily converted into corresponding surfactants—alkyl carbamates. Conditions of their syntheses are truly simple—just stirring and heating reagents in an equimolar ratio without any inert gas protection in a common laboratory flask. Obtained surfactants have surface activity comparable to other nonionic surfactants but they are considerably less toxic and highly biodegradable materials. Hence, these surfactants may have a wide exploitation when the simplicity of their preparation is important.

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