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Novel nonionic siloxane surfactants

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A new method for ethoxylation without application of pressure is described. Butynediol-oligo(oxyethylene) [$H(OCH_2CH_2)_n$—OCH_2—C≡C—$CH_2O(CH_2CH_2O)_nH$ with $n = 1$–16] has been prepared in the presence of an electrophilic catalyst in a specially developed reciruculating apparatus. The products have been characterized by NMR and IR spectroscopy.

New nonionic silicone surfactants have been synthesized by hydrosilylation of these butynediol-oligo(oxyethylenes) with defined siloxanes and polysiloxanes. Protection of the hydroxyl group before hydrosilylation was not necessary. Hydrosilylation was carried out in the presence of a solvent. It has been possible to obtain surfactants with a surface tension of about 21–22 mN m^{-1} and an interfacial tension of 2 mN m^{-1}.

Keywords: surfactants, hydrosilylation, silicone, (poly)siloxanes

INTRODUCTION

Ethoxylated products are an important class of nonionic surfactant. They are used, for example, as wetting agents and polyurethane additives.

The ethoxylation of but-2-yne-1,4-diol (**1**) under a pressure of 5–20 atm has been known for a long time.[1] It was carried out in the presence of basic catalysts, such as sodium hydroxide or triethylamine. But there has always been a side reaction; ketone was obtained by a so-called 'reversed Favorskij reaction'.

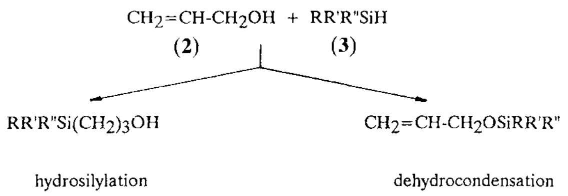
Recently, methods were described for the ethoxylation of acetylenic alcohols at temperatures of 50–60 °C and a pressure of 3–4 atm in the presence of catalysts such as phosphines, basic ion exchangers, dipolar aprotic solvents or thioethylene glycol.[2-4]

Umbach and Stein carried out the ethoxylation of primary and secondary alcohols using carbenium salts as catalysts.[5] They obtained only products with a low degree of ethoxylation. The reaction of saturated or olefinic alcohols and 1–3 mol of ethylene oxide per mol hydrogen was carried out in a temperature range of 70–120 °C under atmospheric pressure and at pressures up to 15 atm. The conversion of alcohol was 70–95%, which was higher than that by reactions in the presence of basic or acidic catalysts. The content of polyglycols formed in these reactions could be reduced to 1–2%.

It is the aim of this paper to propose a new method for the ethyoxylation of but-2-yne-1,4-diol at atmospheric pressure. The degree of ethoxylation has to be high; the amounts of the unreacted but-2-yne-1,4-diol and side products formed have to be reduced to a minimum.

Zaslavskaya and co-workers investigated the hydrosilylation of allyl alcohol (**2**) with several hydrosilanes (**3**) and estimated the activation energy for hydrosilylation ($E_A = 24.9$–67.1 kJ mol^{-1}) and dehydrocondensation ($E_A = 32.5$–97.5 kJ mol^{-1})[6] (Scheme 1).

The activation energy for hydrosilylation of the reactive triple bond should be lower than that for dehydrocondensation because of high association interactions. If the difference between both activation energies can be increased, it should be possible to carry out the hydrosilylation without protection of the hydroxyl group. Such an effect can be envisaged by use of a solvent. The solvation of the hydroxyl group increases the activation energy of the dehydrocondensation.



Scheme 1

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† Dedicated to the memory of Dr G Sonnek.

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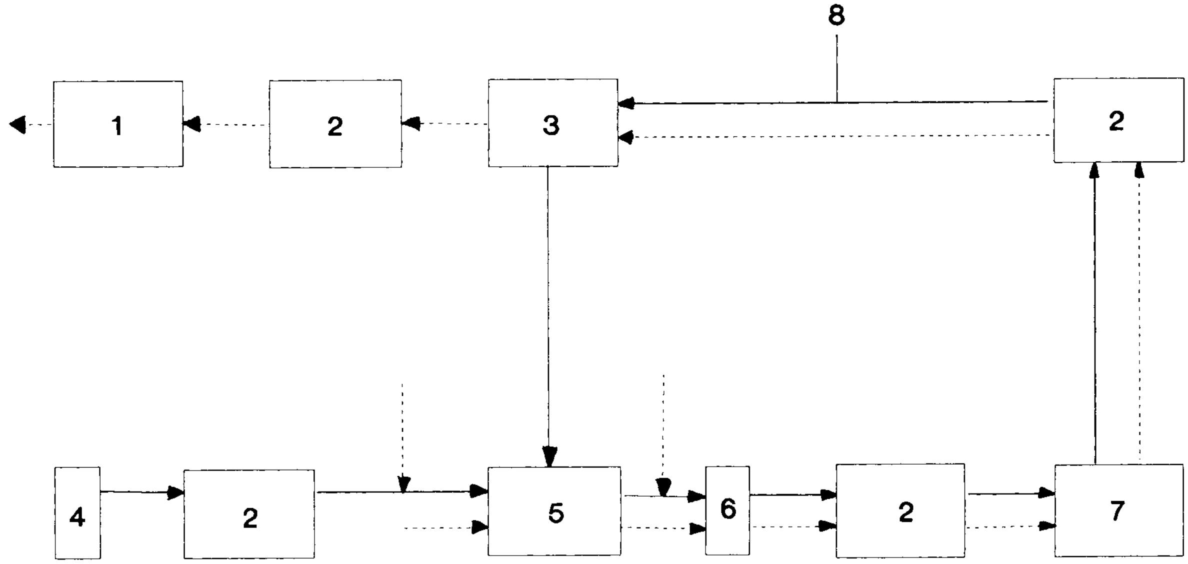


→ Stream of ethylene oxide
-→ Stream of inert gas

1 Pressure compensation
2 Safety flask
3 Ethylene condenser
4 Ethylene oxide flask
5 Ethylene oxide storage vessel
6 Bubble counter
7 Reaction vessel with stirrer, condenser and thermometer in a thermostat
8 Security apparatus

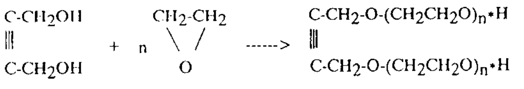
Figure 1 Circuit apparatus for the ethoxylation without applied pressure.

MATERIALS AND METHODS

Preparation

α,α'-But-2-yne-1,4-diyl-bis[ω-hydroxy-oligo (oxyethylene)]

The ethoxylation (Eqn [1]) of but-2-yne-1,4-diol (**1**) was carried out at atmospheric pressure in an apparatus especially developed for the reaction (Fig. 1). This apparatus allows one to control the temperature and the amount of the ethylene oxide (**4**) introduced into the reactor. The ethylene oxide flows from the flask into the storage vessel, and from there through a bubble counter and a safety flask in the reaction vessel equipped with a stirrer, condenser and thermometer. Unreacted ethylene oxide flows to a special ethylene oxide condenser, which is connected with a storage vessel of ethylene oxide. The ethylene oxide is thereby recycled. The reaction can be carried out only under inert conditions. The temperature of the reaction lies between 50 and 90 °C and can be maintained by thermostating the reaction vessel. The flow of ethylene oxide has to be regulated so that there is no condensation in the condenser in the reaction vessel.

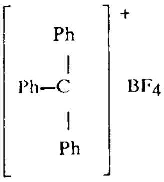


$$\begin{matrix} C\text{-}CH_2OH \\ ||| \\ C\text{-}CH_2OH \end{matrix} + n \begin{matrix} CH_2\text{-}CH_2 \\ \backslash\ / \\ O \end{matrix} \dashrightarrow \begin{matrix} C\text{-}CH_2\text{-}O\text{-}(CH_2CH_2O)_n\text{•}H \\ ||| \\ C\text{-}CH_2\text{-}O\text{-}(CH_2CH_2O)_n\text{•}H \end{matrix} \qquad (1)$$

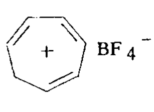
(**1**) (**4**) (**5**)

$n = 1$–16; this, the degree of ethoxylation, is a statistical average value.

In Table 1 the conditions of the reactions and the results of the ethoxylation of but-2-yne-1,4-diol (**1**) are summarized. As catalysts triphenylmethyl tetrafluoroborate (**6**) and cycloheptatrienyl tetrafluoroborate (**7**) were used. The syntheses of these catalysts are described in the literature.[7]



(**6**)



(**7**)

Table 1 Reaction conditions for ethoxylation of butynediol to form **5**

No.	Catalyst Type[a]	 Amount (%)	Reaction temperature (°C)	Reaction time (min)	Degree of ethoxylation, *n* (mol EO/mol OH)[b]	Polydispersity
1	**6**	0.42	70– 90	480	4.5	1.2
2	**6**	0.42	70– 90	540	5	1.5
3	**6**	0.42	80– 90	650	6	1.3
4	**6**	0.42	80–120	840	8	1.4
5	**7**	1.0	70– 90	220	9	—
6	**7**	0.6	70– 90	460	10.4	—
7	**6**	2.0	80– 90	840	12	1.7
8	**6**	1.0	70– 85	410	12.7	—
9	**6**	2.3	65– 85	780	16	1.7

[a] **6**, Triphenylmethyl tetrafluoroborate; **7**, cycloheptatrienyl tetrafluoroborate. [b] The determined degree of ethyoxylation, *n*, is a statistical average value.

Hydrosilylation of α,α′-but-2-yne-1,4-diyl-bis-[ω-hydroxy-oligo(oxyethylene)] with H-siloxanes

The hydrosilylation of α,α′-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo(oxyethylene)] (**4**) is carried out at 100 °C using hexachloroplatinic acid as catalyst *without* protection of the hydroxyl group. Dioxane is applied as solvent. 1,1,1,3,5,5,5-Heptamethyltrisiloxane (**8**) was the preferred H-siloxane. It was obtained by equilibration reaction of hexamethyldisiloxane and NM 203 (a product of Chemiewerk Nünchritz[8]) in the presence of an acidic catalyst.

Hydrosilylation of α,α′-but-2-yne-1,4-diyl-bis-[ω-hydroxy-oligo(oxyethylene)] with polysiloxanes

The hydrosilylation was carried out at 100 °C in dioxane with hexachloroplatinic acid as catalyst. The H-polysiloxanes differ in the sequence and the length of the siloxane chain.

H-polysiloxanes

H-polysiloxanes are obtained by equilibration of hexamethyldisiloxane, NM 203 and cyclosiloxane ((Me_2SiO_n)). The equilibration mixture is stirred for two days at a temperature of 60 °C in the presence of an acidic catalyst. We used Wofatit OK 80 as catalyst. OK 80 is an acidic ion exchanger containing sulphonate groups. Table 2 shows the H-polysiloxanes synthesized and their characterization.

It is also possible to buy H-polysiloxanes from Hüls.

Characterization

^1H NMR spectra were recorded on a Tesla 80-MHz spectrometer, ^{13}C NMR spectra on a Varian XL 300-spectrometer, and ^{29}Si NMR spectra on a Bruker 400 spectrometer. Infrared spectra for the compounds were recorded on a Specord IR 75.

The degree of ethoxylation was determined by measuring the increasing molecular weight, by vapour-pressure osmosis, by the determination of the hydroxyl value, by gel-permeation chromatography and by ^1H NMR spectroscopy.

The surface activity of the substances were determined by de Nouy's version of the ring method.[9] We determined the surface tension in water, the critical micelle concentraion (cmc), the interfacial tension on the n-heptane/water interface, and the contact angle on a paraffin surface and the foam by Ross-Miles method.

RESULTS AND DISCUSSION

Experiments with catalysts described in the literature for the ethoxylation were not successful. Either the but-2-yne-1,4-diol did not react, or glycols were obtained. The reaction temperature

Table 2 Characterization of H-polysiloxanes—$(Me_2SiO)_z$—(MeSiHO)—D_z—D^H

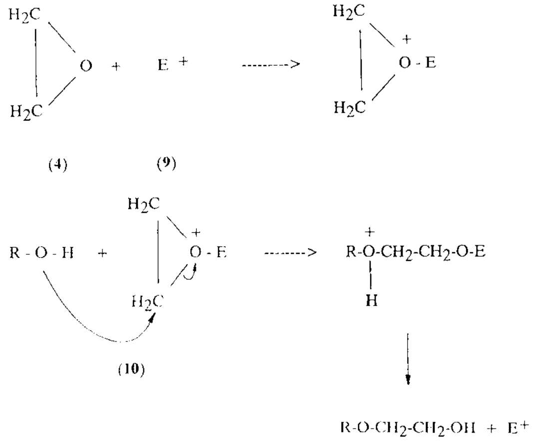
No.	*z*	SiH (%)	Mol. wt
1	1.2	0.683	1 100
2	1.25	0.665	17 000
3	1 36	0.630	9 400
4	1.5	0.592	5 300
5	1.53	0.585	2 270
6	2.43	0.421	17 100
7	2.43	0.422	8 310
8	2.54	0.407	4 510

had to be so high that thermal destruction of the acetylenic bond of the alcohol occurred.

The success of this work depended to a high degree on the type of catalyst used. The selectivity and electrophilicity of the catalyst exert a great influence on the temperature, the degree of conversion and formation of side products. We expected the carbenium salts to be good catalysts because of their Lewis-acid character. We used triphenylmethyl- (**6**) and cycloheptatrienyl tetrafluoroborate (**7**).

The electrophilicity of the catalysts triphenylmethyl tetrafluoroborate (**6**) and cycloheptatrienyl tetrafluoroborate (**7**) is great enough to carry out the reactions at low temperatures. We observed an increase in conversion and selectivity and decreasing formation of side products.

The mechanism of ethyoxylation can be described by Eqns [2]–[4].



(2)

(3)

(4)

The catalyst (**9**) forms an association with the ethylene oxide (**4**). The nucleophilic reagent, in our case butynediol (**3**), attacks the C-atom of the ethylene oxide. There are partial bonds in the activated complex (**10**). The binding between the C- and the O-atoms is broken and the bond between the C-atom and the reagent (butynediol) is formed. The E^+ splits off and the hydrogen atom is added to the oxygen atom.

The NMR spectroscopic characterization of α,α′-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo-(oxyethylene)] is shown in Table 3.

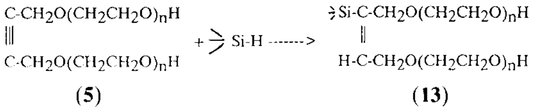
In the ^{13}C NMR spectra, the signals of the α and ω C-atoms are of nearly identical intensity, which means there are no glycols. If there were any glycols, the intensity of the signal of the ω C-atom would be stronger than that of the α C-atom.

It is also possible to detect the glycols by gas chromatography. The peaks of the trimethylsilyl ethers of the ethoxylates behave significantly differently from the trimethylsilyl ethers of the glycols. However, we could not find any glycols. Unreacted alcohol is only found at a low degree of ethoxylation at an amount of about 1%.

The products are slightly yellow, viscous substances. The viscosity depends on the degree of ethyoxylation. An increase in ethylene oxide units per hydroxyl group leads to an increased viscosity. The products are soluble in water, alcohol, acetone and methylene chloride.

It is possible to prepare products with more than 30 ethylene oxides per alcohol.

To obtain nonionic siloxane surfactants, the α,α′-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo-(oxyethylene)] (**5**) has to react with the silicon compound. Hydrosilylaton is a well-known reaction. The hydrosilylation of α,α′-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo(oxyethlene)] (**5**) was carried out first with defined H-siloxanes (Eqn [5]).



(5)

The NMR investigations confirm the structure of α,α′[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]-bis[ω-hydroxy-oligo(oxyethylene)] (**13**) (Table 4).

Table 3 NMR characterization of α,α′-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo(oxyethylene)]

	Chemical shift (ppm)				
	$—CH_2—$	$—CH_2O—$			
^1H NMR	4.14–4.18	3.46–3.53			
	$C\equiv C$	$—CH_2—CH_2OH$	$—(CH_2—CH_2O)_n$	$—CH_2—OH$	$\equiv C—\underline{C}H_2O$
^{13}C NMR	82.14–83.66	71.33–71.36	71.05–71.08	61.83–61.90	58.61–58.69

Table 4 NMR characterization of α,α'-[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]-bis[ω-hydroxy-oligo(oxyethylene)]

	Product chemical shift (ppm)				
	$Si-CH_3$	$-CH_2O-$	$-CH_2-$	$C-H$	
^{1}H NMR	0.1–0.3	3.31–3.33	3.93–3.99	6.1–6.3	
	$-\underline{C}H_2-OH$	$-(CH_2CH_2O)_n$	$-\underline{C}H_2-OH$	$-C{=}C-Si-$	$-C{=}C-H$
^{13}C NMR	61.82–61.88	71.06–71.15	73.31–73.45	138.00–139.00	140.14–141.17
	Me_3SiO	$Si-C{=}CH$			
^{29}Si NMR	8.4–6.4	$-34.0 \cdots -40$			
	Starting matrial chemical shift (ppm)				
	$\equiv C-\underline{C}H_2O$	$C\equiv C$			
^{13}C NMR	58.12–58.72	83.14–83.18			

The C—H shows a triplet at 6.1–6.3 ppm. The new built C—H bond shows a triplet at 6.1–6.3 ppm in the ^{1}H NMR spectrum. The double bond of the C-atom can be identified without any doubt in the ^{13}C NMR spectrum. The signal for the carbon atom attached to the silicon atom appears at 138–139 ppm, the carbon bound to hydrogen at 140–141 ppm. In the IR spectrum we could not find a signal from the Si—H bond at 2160 cm^{-1} (Table 5).

The preparation of the defined H-siloxanes is very expensive. It was therefore an aim of our work to carry out hydrosilylation of α,α-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo(oxyethylenes)] using polymeric H-siloxanes (**14**) (Scheme 2). These poly-H-siloxanes can be easily produced. Various polysiloxanes have been applied which differ in sequence and length of the siloxane chain. The oligo[oxy{1,4-bis[ω-hydroxy-oligo-(oxyethylene)]but-2-ene-2-yl-methylsilylene}-oligo-(dimethylsilylene)] obtained (**15**) was characterized by ^{1}H and ^{13}C NMR and IR spectroscopy (Table 6).

All products possess a good solubility in water and they are readily and clearly soluble in toluene, benzene, tetrachloromethane, trichloromethane, dichloromethane and alcohol. In chlorinated and aromatic solvents the products foam well, but in water there is weak foam formation.

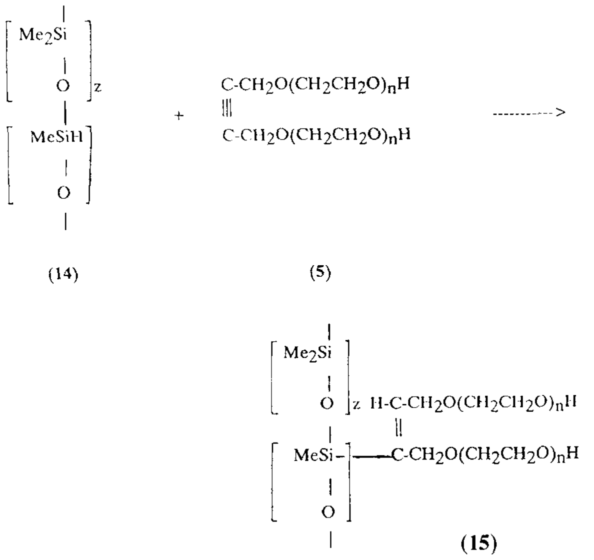
The results show that the intention to carry out hydrosilylation without protection of the hydroxyl group was justified. By application of a solvent, the difference in the activation energies between hydrosilylation and dehydrocondensation routes can be increased so that hydrosilylation of the reactive triple bond is preferred. High association of the hydroxyl group in the polyether chains, forming a so-called random coil, is an explanation for this fact. So the end-group protects itself against the attack of the H-siloxanes.

The advantages of this method are the following: it is successful without a silylation reagent, it has short reaction times using a single-step process that is easily controllable and produces no side-products, and there is the possibility of regulating the reaction temperature by the application of a solvent.

The surface activity data of the synthesized

Table 5 IR characterization of α,α'[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]bis[ω-hydroxy-oligo(oxyethylene)]

—OH—	—C—H—	—C=C—	—CH—	—Si—C—	—Si—H
3300–3466	2893–2656	1713–1726 1613–1629	1240–1255	826–842	—



Scheme 2

α,α'-[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-but-2-ene-1,4-diyl]-bis[ω-hydroxy-oligo-(oxyeth-ylenes)] are shown in Table 7.

The expected correlation between increasing CMC values and the degree of ethoxylation was proved. The surface-tension σ values are equilibrium values. They are corrected after the Harkins–Jordan method.[10] Values lie between 21 and 25 mN m^{-1}. Taking into account the surface-tension values of the nonhydrosilylated adducts of about 40 mN m^{-1}, the striking influence of the siloxane blocks can be well estimated. The influence of the siloxane blocks is significantly higher than that of alkyl or phenylalkyl groups, because their surface tension reaches values of about 27 mN m^{-1}

The interfacial tension was measured at the water/n-heptane interface γ. The interfacial tensions are very low and increase with increasing degree of ethyoxylation. Unlike the wetting ability, the foam term is not very high. An expression of wetting ability is the contact angle θ_{par}. It was measured on paraffin. The Hydrophilic–Lipophilic-Balance value (HLB)[11] value increases with increasing degree of ethoxylation.

The surface-active data of the oligo[oxy{1,4-bis[ω-hydroxy-oligo(oxyethylene)]but-2-enyl-methylsilylene}oligo-oxy(dimethylsilylene)] (**15**) in relation to the siloxane group and the alkylene-oxide compounds are shown in Table 8. The physico-chemical properties of the siloxane-modified butynediol–ethylene oxide adducts can be influenced by varying the sequence and the

Table 6 NMR and IR characterization of oligo[oxy{1,4-bis[ω-hydroxy-oligo(oxyethylene)]but-2-ene-2-yl-methylsilylene}oligo-oxy(dimethylsilylene)]

	Product chemical shift (ppm)				
	Si—CH$_3$	—CH$_2$O—	—CH$_2$—	—C—H	
^{1}H NMR	0.1–0.3	3.30–3.32	3.94–3.98	6.1–6.3	
	—C=C—H	C=C—Si	CH$_2$CH$_2$—OH	(CH$_2$CH$_2$O)$_n$	CH$_2$—OH
^{13}C NMR	141.1–141.2	138.5–139.5	73.7–73.82	70.96–71.06	61.6–61.87

For comparison:

	Starting material chemical shift (ppm)	
	≡C—CH$_2$OH	C≡C
^{13}C NMR	58.66–58.72	83.12–83.18

	Si—H	Si—CH$_3$	Si—C
Product IR stretching vibration (cm^{-1})	—	1243	840

Table 7 Surface activity of α,α'-[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]bis[ω-hydroxy-oligo(oxyethylene)]

Degree of ethoxylation (mol EO/mol OH)	4.5	5	6	8	9	10	12	16
Mol. wt	700	760	840	1010	1100	1290	1360	1494
cmc × 10^5 mol dm^{-3}	3.3	5.2	6.1	9.4	9.5	11.0	11.0	15.0
σ_{cmc} (mN m^{-1})	22.0	25.0	24.7	22.0	21.8	21.0	21.0	22.0
γ_{max} (mN m^{-1})	0	1.0	6.0	4.3	2.5	2.0	3.0	2.0
θ_{par} (grd)	Spreads	26.8	53.4	38.9	21.3	21.5	Spreads	22.1
Foam capacity (%)	No foam	53.3	31.6	29.4	28.2	27.8	No foam	27.3
Foam stability (%)	—	10.4	85.7	86.2	88.0	88.3	—	88.9
HLB value	12.3		12.6		13.4		18.8	19.0

length of the siloxane chain and the ethylene oxide chain.

If the ratio of the dimethylsiloxy units to ethylene-oxide-substituted siloxane units was about 2.5:1, then the values for the surface tension were found to reach 30–34 mN m^{-1}.

Solubility in water is lowered by bulky hydrophobic siloxane groups. Decrease of the ratio of dimethylsiloxy units to ethylene-oxide-substituted siloxane units should improve the water solubility, and the surface tension should be lower. If the siloxane chain length is decreased, the water solubility increases and the values of surface tension of the siloxane-substituted butynediol–ethylene oxide adducts decrease. This phenomenon can be explained by a better orientation of the molecules with shorter chains at the interface.

Also, a decrease of the ethylene oxide chain length leads to a decrease of surface tension.

Thus it is possible to synthesize nonionic silicon surfactants by hydrosilylation of α,α'-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo(oxyethylene)] with polymer H-siloxanes, giving a surface tension of about 22 mN m^{-1} and an interfacial tension of about 2 mN m^{-1}

SUMMARY

We have developed a new method for the ethoxylation of but-2-yne-1,4-diol at atmospheric pressure. This reaction was carried out at low temperatures (60–85 °C) in the presence of an electrophilic catalyst.

Clear yellow, viscous oils which are readily soluble in water, alcohol, acetone and methylene chloride were obtained. The viscosity depends on

Table 8 Surface activity of oligo [oxy{1,4-bis[ω-hydroxy-oligo(oxyethylene)]but-2-ene-2-yl-methylsilylene}oligo-oxy(dimethylsilylene)] (**15**)

n	z	Mol. wt of polysiloxane (g mol^{-1})	σ_{cmc} (mN m^{-1})	cmc × 10^4 (mol dm^{-3})	γ (mN m^{-1})	θ_{par} (grd)	Foam after 2 min (cm)
In relation to polysiloxane:							
15.3	2.54	4510	34.9	59.6	12.2	76.4	0.0
7.8	2.54	4510	30.3	126.0	9.1	61.7	0.0
7.8	1.53	2270	29.5	3.32	6.5	55.8	0.8
7.8	1.2	1100	22.9	1.25	2.0	19.3	5.0
7.8	M_2D^{H} [a]	222.5	22.0	7.38	1.2	10.6	8.0
In relation to ethylene oxide:							
15.3	1.53	2270	30.9	3.43	10.5	57.6	0.8
12.7	1.53	2270	31.5	2.76	9.6	55.6	0.8
7.8	1.53	2270	29.5	3.32	6.5	55.8	0.8
4.8	1.53	2270	22.9	1.81	3.0	29.8	1.0

[a] M_2D^{H}, 1,1,1,3,5,5,5-heptamethyltrisiloxane.

the degree of ethoxylation. It is possible to obtain products with more than 30 mol of ethylene oxide per mol of alcohol.

We have prepared novel nonionic siloxane surfactants by hydrosilylation of α,α'-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo(oxyethylenes)] with H-siloxanes in the presence of a platinum catalyst. We have shown that it is possible to carry out the hydrosilylation without protection of the hydroxyl group in the presence of a solvent. There is no attack on the hydroxyl group.

These products have excellent surface-active properties. The surface tension reaches values of about 21–22 mN m^{-1}.

Hydrosilylation was carried out with defined H-siloxanes and, as an alternative, with polysiloxanes. The polysiloxanes can be easily prepared.

The surface-active properties of the oligo-[oxy{1,4-bis-[ω-hydroxy-oligo(oxyethylene)]but-2-ene-2-yl-methylsilylene}oligo-oxy(dimethylsilylene)] were investigated in relation to the siloxane block and the degree of ethoxylation. It is possible to obtain surfactants with a surface tension of 22 mN m^{-1}.

A decrease of the ethylene oxide and a simultaneous decrease of the sequence and length of the siloxane chain leads to a decrease in surface tension.

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