Journal of Organometallic Chemistry, *446* (1993) 9–13

JOM 22918

Short Review

Organosiloxanes with functional groups – a short review *

G. Schmaucks, R. Wagner and R. Wersig

Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Institutsteil Adlershof, Rudower Chaussee 5, O-1199 Berlin (Germany)

(Received April 22, 1992)

1. Introduction

In this review we summarize some of the results of our investigations in recent years. The aim of our work is to provide an explanation of the extraordinary surface activity of silicon compounds. We report the synthesis of defined siloxane compounds with various functional groups and various different spacers between the hydrophobic siloxane group and the hydrophilic functional group, and the investigation of adsorption behaviour. Figure 1 depicts the three types of species we have studied in recent years, namely siloxane derivatives of dicyclopentadiene, nonionic silicon surfactants based on butynediol, and nitrogen-containing cationic siloxanes.

2. Siloxanylpropylammonium halides

N-alkyl-*N*,*N*-dimethyl-3-(siloxanyl)propyl ammonium halides of the general formula $(Me_3SiO)(SiMe_2O)_nSiR^1R^2(CH_2)_3N^+Me_2R^3X^-$ (R^1,R^2 = Me, $OSiMe_3$; $n = 0, 1$; R^3 = alkyl or alkenyl; X = halogen) were prepared by hydrosilylation of *N*,*N*-dimethylallylamine with pentamethyldisiloxane (**1a**), 1,1,3,3,5,5,5-heptamethyltrisiloxane (**1b**), 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1c**) and tris-trimethylsiloxy-silane (**1d**) in the presence of divinyltetramethyldisiloxane platinum complex [1] as catalyst, followed by quaternization with alkyl halides. The ratio of β- to γ-isomer depends on the *H*-siloxane (**1a–d**) used. More sterically hindered siloxanes give more γ-addition (Table 1) because of their lower reactivity. No side reactions or by-products were observed. Surprisingly we found that quaternization of the γ-product was preferred when the mixture with the β-isomer was used for the reaction (Fig. 2). This can be attributed to steric hindrance to the attack of the alkyl group on the nitrogen atom by the bulky siloxanyl group attached to the β-carbon atom. Table 2 shows the spectroscopic evidence that the investigated quaternary ammonium compounds are exclusively derivatives of the γ-isomers. If the 2-siloxanylaminopropane is separated by distillation, it can also be quaternized, but the reaction time required is much longer (about 20 h instead of 8 h).

The quaternary ammonium compounds are hygroscopic crystalline white solids with good solubility in water and most organic solvents. The crystal structures of *N*,*N*-dimethyl-*N*-propyl-3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propylammonium bromide (**5c**) and *N*-butyl-*N*,*N*-dimethyl-3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propylammonium bromide (**5d**) were determined by X-ray crystallography [2] and showed no significant differences. The bond distances and angles and one layer in the crystal lattice are shown in Fig. 3.

The adsorption behaviour was studied by surface tension measurements using the ring method in the version of du Noüy. The results are given in Table 3. The required surface area per molecule was calculated by use of the Frumkin isotherm [3].

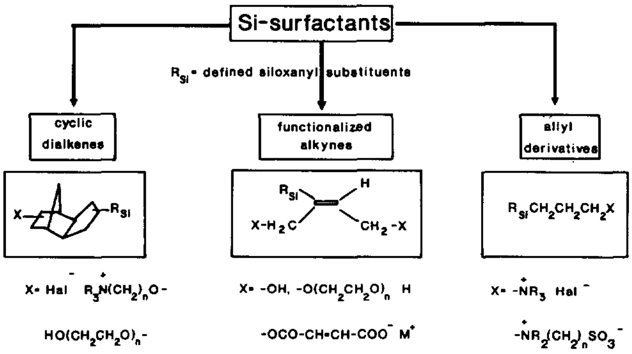

Fig. 1.

Correspondence to: Dr. G. Schmaucks.

* Dedicated to Professor M.G. Voronkov in recognition of his important contributions to organosilicon chemistry.

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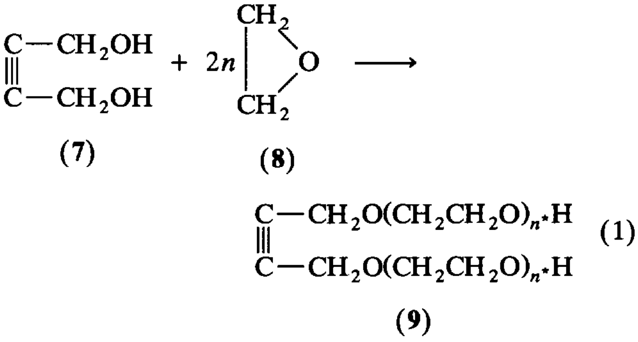
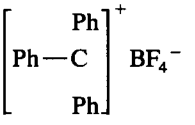
It is evident that variation of the siloxanyl group has a significant effect on the surface tension depression and on other data.

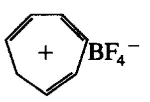
3. Functionalized alkynes

The α,α'-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo(oxyethylene)] species (**9**) are the starting materials for novel nonionic siloxane surfactants. It is possible to carry out the ethoxylation of but-2-yne-1,4-diol (**8**) at atmospheric pressure and at low temperatures (60–85°C) by using carbenium salts such as triphenylmethyltetrafluoroborate (**10**) and cycloheptatrienyltetrafluoroborate (**11**) as catalysts.


(7) (8) (9) (1)

(n^* is a mean value)


(**10**)

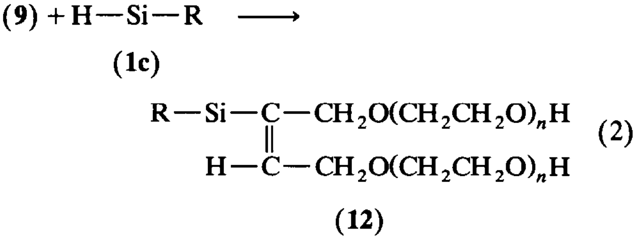

(**11**)

It is possible to prepare products with more than 30 mol of ethylene oxide per mol of alcohol [4]. The NMR spectra show no evidence for formation of glycols. The products are slightly yellow viscous substances. The viscosity increases with the degree of ethoxylation.

TABLE 1. Hydrosilylation of N,N-dimethylallylamine with H-siloxanes (**1a**–**1d**) to give siloxanylpropylamines (**2a**–**2d**)

H-Siloxane	Reaction time (h)	B.p. (°C/kPa)	Yield (%)	Ratio of γ- to β-isomer (%)		
1a $Me_3SiOSiMe_2H$	1	83/1.8	80	87.5	12.5	**2a**
1b $Me_3Si(OSiMe_2)_2H$	8	109/1.8	83	88	12	**2b**
1c $(Me_3SiO)_2SiMeH$	8	102/2.0	85	85	15	**2c**
1d $(Me_3SiO)_3SiH$	12	126/2.0	80	100	0	**2d**

The reaction of α,α'-but-2-yne-1,4-diyl-bis[ω-hydroxy-oligo(oxyethylene)] (**9**) with 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1c**) to α,α'-[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]bis[ω-hydroxy-oligo(oxyethylene)] (**12**) was carried out in the presence of a platinum catalyst. In the ^{13}C NMR spectra of the products, instead of the signals of the triple bond at about 83 ppm and 58 ppm there are the signals of the double bond at about 140–141 ppm and 138–139 ppm. (Fig. 4). The Si-H band at 2160 cm^{-1} has disappeared from the IR spectrum.


(2)

$$(9) + \underset{(1c)}{H{-}Si{-}R} \longrightarrow \underset{(12)}{\begin{array}{l} R{-}Si{-}C{-}CH_2O(CH_2CH_2O)_nH \\ \quad\;\; H{-}C{-}CH_2O(CH_2CH_2O)_nH \end{array}} \qquad (2)$$

The α,α'-[2-[1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]bis[ω-hydroxy-oligo(oxyethylenes)] are substances with excellent surface active properties. The surface tension reaches values of 21–22 mN m^{-1}.

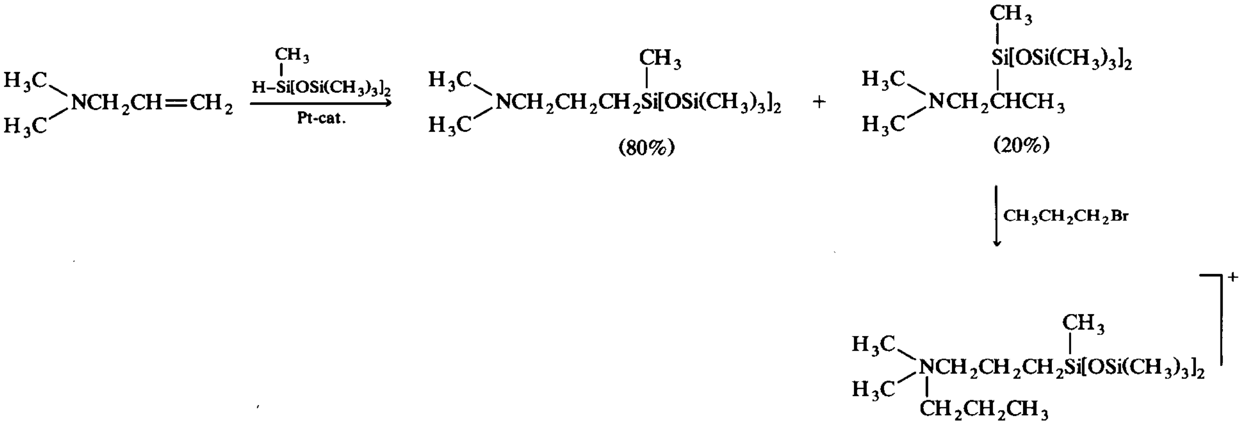
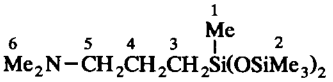
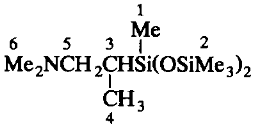
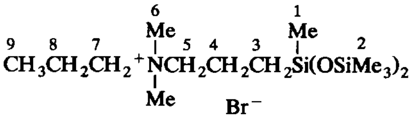


Fig. 2. Reaction schemes in the synthesis of the siloxanylpropylammonium halides.

TABLE 2. ^{13}C-NMR spectra data of siloxy aminopropanes

Formula		^{13}C-NMR spectra data (ppm)
2c	 $\overset{6}{Me_2}N-\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{\overset{1}{Me}}{Si}\overset{2}{(OSiMe_3)_2}$	$-0.53(1)$; 1.61(2); 15.04(3) 21.14(4); 62.96(5); 45.25(6)
2'c	 $\overset{6}{Me_2}N\overset{5}{C}H_2\underset{\underset{4}{CH_3}}{\overset{3}{C}H}\overset{\overset{1}{Me}}{Si}\overset{2}{(OSiMe_3)_2}$	$-2.01(1)$; 1.64(2); 19.99(3) 11.80(4); 61.62(5); 45.15(6)
5c	 $\overset{9}{C}H_3\overset{8}{C}H_2\overset{7}{C}H_2{}^+\underset{Me}{\overset{\overset{6}{Me}}{N}}\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{\overset{1}{Me}}{Si}\overset{2}{(OSiMe_3)_2}\ Br^-$	$-0.18(1)$; 1.92(2); 13.13(3) 16.92(4); 65.26(5); 51.46(6) 66.26(7); 16.48(8); 10.74(9)

The influence of the siloxane block is significantly higher than that of the alkyl or phenylalkyl group, which lower surface tensions only reaches to about 27 mN m^{-1}. Since the surface tensions of the nonhydrosilylated adducts are about 40 mN m^{-1} the striking influence of the siloxane block is evident.

TABLE 3. Interfacial activity of alkyl-*N*,*N*-dimethyl-3-(siloxanyl)propyl ammonium halides

Compound	Alkyl group	concn. (mol/l)	Maximum surface tension tension depression (mN m^{-1})	Interfacial tension cv > cmc (mN m^{-1})	Contact angle c > cmc (deg)	Foam ability 5 g l^{-1} Bartsch-Tube (cm)	Surface area per molecule (Å^2)
Disiloxanes $Me_3SiOSiMe_2(CH_2)_3N^+Me_2R\ Br^-$							
3b	C_2H_5	6.9×10^{-2}	26.5	4.5	48.9	0	34.2
3c	C_3H_7	2.6×10^{-2}	23.5	1.8	55.4	0.3	43.1
3d	C_4H_9	5.7×10^{-2}	24.6	2.7	33.4	0	47.4
Straight chain trisiloxanes $Me_3SiOSiMe_2OSiMe_2(CH_2)_3N^+Me_2R\ Br^-$							
4b	C_2H_5	2.3×10^{-2}	20.4	1.1	spr [a]	2.0	44.2
4c	C_3H_7	9.7×10^{-3}	19.0	1.0	spr	13.0	43.1
4d	C_4H_9	1.0×10^{-2}	20.0	*ca.* 0	spr	14.0	45.1
Branched trisiloxanes $(Me_3SiO)_2SiMe(CH_2)_3N^+Me_2R\ X^-$							
5a	CH_3	1.4×10^{-2}	22.5	–	–	–	64.6
5b	C_2H_5	2.2×10^{-2}	20.6	*ca.* 0	spr	0	58.9
5c	C_3H_7	2.0×10^{-2}	20.2	1	spr	0	64.6
5d	n-C_4H_9	9.6×10^{-3}	18.5	*ca.* 0	spr	12.0	62.8
5e	i-C_4H_9	1.3×10^{-2}	21.6	–	–	–	61.2
5f	allyl	2.4×10^{-2}	19.5	*ca.* 0	spr	0	63.2
5g	CH_3	2.2×10^{-3}	30.7	–	–	–	59.0
5h	allyl	2.1×10^{-2}	24.0	*ca.* 0	spr	0	60.5
Branched tetrasiloxanes $(Me_3SiO)_3Si(CH_2)_3N^+Me_2R\ Br^-$							
6a	CH_3	4.5×10^{-3}	22.4	–	–	–	69.9
6b	C_2H_5	2.4×10^{-3}	17.9	1	spr	15.0 [b]	69.4
6c	C_3H_7	2.8×10^{-3}	18.8	*ca.* 0	spr	17.5 [b]	77.9
6d	n-C_4H_9	2.6×10^{-3}	19.3	*ca.* 0	spr	12.0 [b]	76.6
6f	allyl	2.9×10^{-3}	18.4	*ca.* 0	40.0	19.0 [b]	74.5

[a] spr refers to spreading of a drop of water on paraffin surface. [b] Foaming ability as determined by the method of Ross–Miles in (%) at a concentration of 3 g l^{-1}.

	ability	stability
6b	156.2	89.9
6c	164.0	89.7
6d	128.0	93.9
6f	171.9	91.0

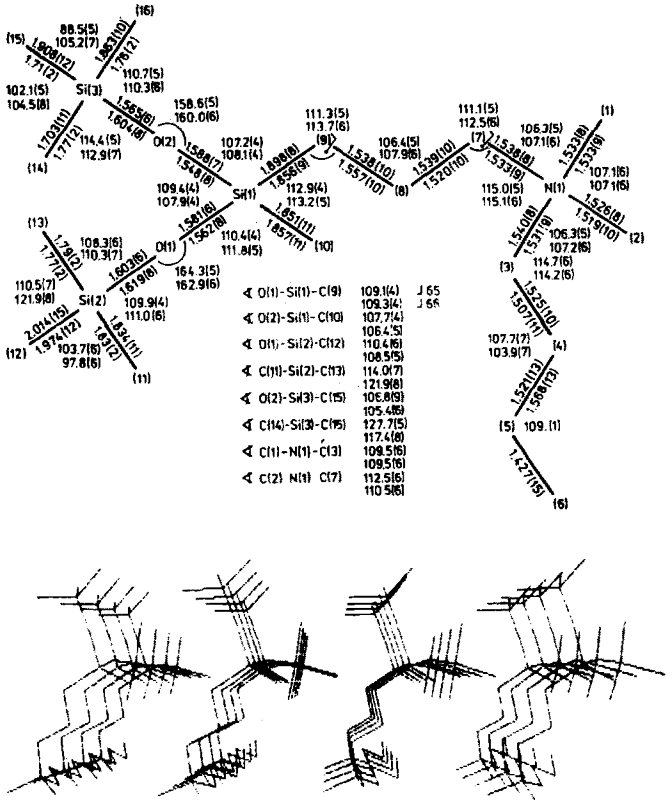


Fig. 3. Crystal structure of alkyl-*N*,*N*-dimethyl-3-(siloxanyl)propylammonium bromides.

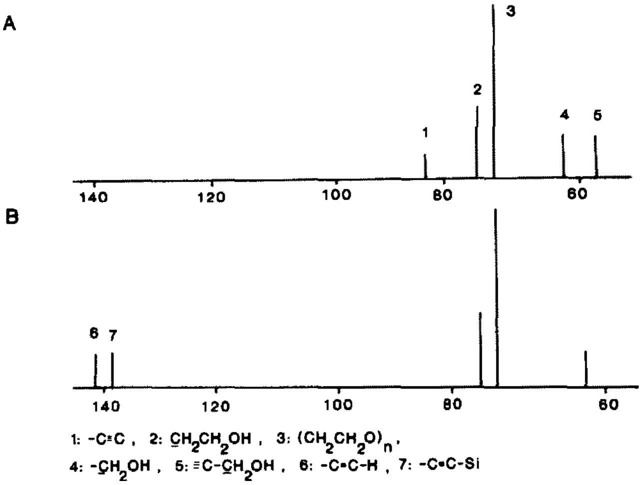


Fig. 4. ^{13}C NMR spectra of α,α'-but-2-yne-1,4-diyl[ω-hydroxy-oligo(oxyethylene)] (**A**) and α,α'-[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]bis[ω-hydroxy-oligo(oxyethylene)] (**B**).

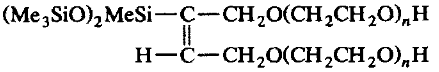
In Table 4 are summarized the surface activity data for α,α'-[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]bis[ω-hydroxy-oligo(oxyethylene)].

4. Siloxanyl modified derivatives of dicyclopentadiene

In contrast to allylamines and butyne-1,4-diol the dicyclopentadiene entity possesses two double bonds that may undergo hydrosilylation. This hydrosilylation of dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene) with *H*-silanes/siloxanes selectively yields norbornene-ring substituted 5(6)-silyl/siloxanyl-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-indene species [5,6] and only by use of the most reactive chlorosilanes under vigorous conditions was it possible to synthesize 2(3),5(6)-disilylated products [7].

In contrast, of dihalocarbene additions the only one known that selectively blocks the less reactive cyclopentene ring double bond yields dihalocyclopropane structures [8], which can undergo rearrangements thermally and in the presence of electrophiles. This is why the dihalocyclopropane species as well as the long-known norbornene ring halogen [9], ether [10,11] and ester [12] derivatives of dicyclopentadiene have never been used before as precursors in hydrosilylation reactions. As we expected, addition of H-silanes/siloxanes to the dichlorocarbene product proceeded under mild

TABLE 4. Surface activity data for α,α'-[2-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)but-2-ene-1,4-diyl]bis[ω-hydroxy-oligo(oxyethylene)]



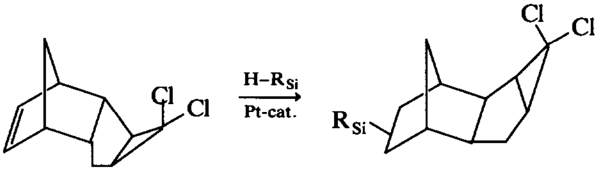
$$\begin{array}{l}(Me_3SiO)_2MeSi{-}C{-}CH_2O(CH_2CH_2O)_nH\\ \qquad\qquad\quad \| \\ \qquad\qquad H{-}C{-}CH_2O(CH_2CH_2O)_nH\end{array}$$

Degree of ethoxylation (mol EO/OH)	Moleculare weight (g mol^{-1})	cmc 10^5 (mol l^{-1})	Surface tension σ_{cmc} (mN m^{-1})	Interfacial tension γ_{cmc} (mN m^{-1})
6	840	6.1	24.7	6.0
8	1010	9.4	22.0	4.3
10	1290	11.0	21.0	2.0
12	1360	11.0	21.0	2.0
16	1494	15.0	22.0	2.0

TABLE 5. Critical micelle formation concentration and surface tension

R	cmc ($mol\,l^{-1}$)	σ ($mN\,m^{-1}$)
$HO(CH_2CH_2O)_6$	3.7×10^{-4}	28.6
$HO(CH_2CH_2O)_{12}$	1.2×10^{-4}	23.8

conditions to yield the 3(4)-silyl/siloxanyl derivatives of 1,1-dichloro-1,1a,1b,2,3,4,5,5a,6,6a-decahydro-2,5-methanocycloprop-α-indene [13,14] (eqn. (3)).

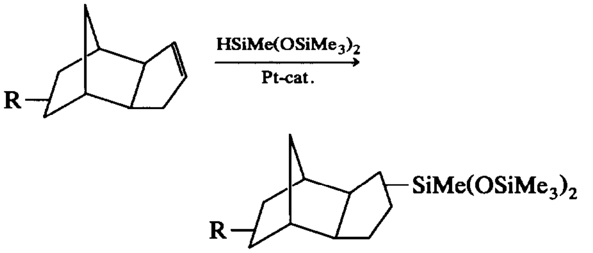


(3)

(R_{Si} = $[(CH_3)_3SiO]_2CH_3Si$–; $(CH_3)_3SiO(CH_3)_2Si$–; $(C_2H_5O)_3Si$–; $(CH_3)_2ClSi$–; CH_3Cl_2Si–; Cl_3Si–)

The products are mixtures of two isomers, which were shown to be the *exo*-3 and *exo*-4 addition products [15]. Fortunately all of the products appeared to be stable during the distillation, and this should open the way to adequate functionalization of the dichlorocarbene unit.

The catalytic addition of 1,1,1,3,5,5,5-heptamethyltrisiloxane to various norbornene ring-functionalized dicyclopentadiene precursors under relatively convenient conditions yields a remarkable variety of 2(3)-(1,1,1,3,5,5,5-heptamethyltrisiloxanyl)-5(6)-halogen, ether, or other derivatives of 2,3,3a,4,5,6,7,7a-octahydro-4,7-methano-1*H*-indene [16,17] (eqn. (4)).



(4)

(R = $HO(CH_2CH_2O)_n$– (Reactions with $(CH_3)_3Si$–protected OH– groups) n = 0,1,2,3,4,6,12; Cl–, Br–; $ClCH_2COO$–; $ClCH_2CH_2O$–, $ClCH_2CH_2OCH_2CH_2O$–; $ClCH_2CH_2CH_2O$–; CH_3O–, $CH_3CH_2OCH_2CH_2OCH_2CH_2O$–)

A detailed GC-MS investigation of the methoxy product showed that the addition of the H–Si bond took place in the four stereochemically possible *exo*-2, *endo*-2, *exo*-3 and *endo*-3 positions.

All above mentioned halogenated siloxanyl species should be potential precursors for the synthesis of N-containing surfactants but the polyalkoxy products themselves possess surface active properties (Table 5). In comparison to the data for the ethoxylated butyne-1,4-diol products, these initial data reveal an increase in lyophilic properties with maintainance of the siloxane-specific low surface tension values.

5. Conclusions

The surface activity measurements show the significant influence of siloxanyl groups on the interfacial parameters. The extent of surface tension depression is greater than that found for hydrocarbon surfactants. The surface activity and other properties, for instance the solubility, also depend on the spacer connecting the hydrophobic and hydrophilic groups. In our opinion this effect is mainly determined by the possible arrangement of the molecules at the interface.

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