Syntheses and Properties of Surfactants Containing Organometals: IV. Organo Silicone

HIROHISA MAKI, SHYUJI SAEKI, ISAO IKEDA and SABURO KOMORI,
Faculty of Engineering, Osaka University, Yamadakami, Suita City, Osaka, Japan

Abstract

The authors synthesized nonionic surfactants containing dimethylpolysilane, dimethylpolysilmethylene and dimethylpolysiloxane as the hydrophobic groups, and investigated their surface activities. In their ability to lower the aqueous surface tension, the polysiloxane surfactants were the most active, and there is little reason to choose between the other two kinds of surfactants. With regard to the ability of lowering the interfacial tension between water and silicone oil, the polysilmethylene surfactants were most effective when the concentration of aqueous solution was below 0.5 wt %. Above this concentration, however, the polysiloxane surfactants were superior. Also investigated was the lowering of surface tension of nonaqueous polyols and their ability to wet low energy hydrophobic surfaces such as polyethylene.

Introduction

Recently, surfactants containing silicon atoms in the main chain have been synthesized and their several interesting properties have been reported.

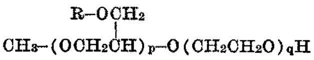
Kanner et al. (1), for example, synthesized the nonionic surfactants containing dimethylsiloxane which are represented by Equation 1, and reported that these had interesting properties as surfactants (1).

$$(CH_3)_3Si\left(OSi(CH_3)_2\right)_n(CH_2)_3O(CH_2CH_2O)_mCH_3 \qquad [1]$$

We previously reported the synthesis of cationic surfactants [2] from monochlorinated dimethylpolysiloxane and secondary amine (2), and of the nonionic surfactants [3] from glycidyl ethers having a series of dimethylpolysiloxane groups.

$$(CH_3)_3Si\left(OSi(CH_3)_2\right)_nCH_2NR_2\cdot HCl \qquad [2]$$

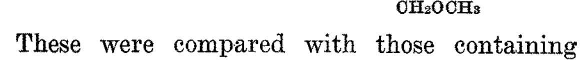
These were compared with the above mentioned Kanner's surfactants (3).



$$CH_3{-}(OCH_2\underset{}{\overset{\overset{\textstyle R{-}OCH_2}{|}}{C}}H)_p{-}O(CH_2CH_2O)_qH \qquad [3]$$

R = Propyl group containing dimethylpolysiloxane.

As surfactants containing polysilmethylene groups as the hydrophile have scarcely been investigated, we synthesized the nonionic surfactants which are represented by Equation 4 (4).



$$(CH_3)_3Si\left(CH_2Si(CH_3)_2\right)_n(CH_2)_3OCH_2\underset{\underset{\textstyle CH_2OCH_3}{|}}{C}HO(CH_2CH_2O)_mH \qquad [4]$$

These were compared with those containing dimethylpolysiloxane groups of a similar type to Equation 4, and it was found that the ability of lowering the aqueous surface tension was inferior to that of the polysiloxane derivatives.

This time, the authors have synthesized a new kind of nonionic surfactantants containing dimethylpolysilane, and have compared them with polysilmethylene surfactants

$$(CH_3)_3Si\left(CH_2Si(CH_3)_2\right)_n(CH_2)_3O(CH_2CH_2O)_mH \qquad [6]$$

and polysiloxane surfactants

$$(CH_3)_3Si\left(OSi(CH_3)_2\right)_n(CH_2)_3O(CH_2CH_2O)_mH \qquad [7]$$

of a type analogous to Equation 5. The synthesis consisted of the following steps:

$$(CH_3)_3Si\left(Si(CH_3)_2\right)_nH + CH_2=CHCH_2OSi(CH_3)_3 \xrightarrow[\text{DTBP catalyst}]{}$$

$$(CH_3)_3Si\left(Si(CH_3)_2\right)_n(CH_2)_3OSi(CH_3)_3 \xrightarrow{H_2O}$$

$$(CH_3)_3Si\left(Si(CH_3)_2\right)_n(CH_2)_3OH \xrightarrow[BF_3\cdot Et_2O\text{ catalyst}]{EO}$$

$$(CH_3)_3Si\left(Si(CH_3)_2\right)_n(CH_2)_3O(CH_2CH_2O)_mH \qquad [5]$$

The effects of the hydrophile on the surface activities in these samples were then investigated.

Since the Si-Si bond is split by an alkali or an amine, $BF_3\cdot Et_2O$ was used as the catalyst in the reaction of ethylene oxide with the alcohol containing polysilane.

Experimental Procedures

Syntheses of Dimethylpolysilane Nonionic Surfactants (V)

Preparation of $(CH_3)_3Si\left(Si(CH_3)_2\right)_n(CH_2)_3OSi(CH_3)_3$ (V') (n = 1,2). Pentamethyldisilane and heptamethyltrisilane were prepared from trimethylchlorosilane and dimethyldichlorosilane by the method of Kumada et al. (5).

After sweeping the system with nitrogen, 0.23 moles of trimethylallyloxysilane were charged to a 50 ml four necked flask fitted with a stirrer, a thermometer, a pressure equalizing dropping funnel, a gas inlet tube and a reflux condenser. In the dropping funnel was placed 2.2 g (0.015 mole) of di-tert-butyl peroxide dissolved in a further portion of trimethylallyloxysilane (0.11 mole). The mixture in the reaction flask was heated to reflux and then the contents of the dropping funnel were added dropwise by stirring. After complete addition of the peroxide solution, the reaction mixture was refluxed for 40 hr during which time the reflux temperature increased to 104 C (125 C in the case of trisilane). After cooling, the product was fractionally distilled under reduced pressure.

In the case of m = 1, the product V (bp = 70 C/1.5 mm Hg, n_D^{20} = 1.4475, molar refraction calculated = 84.69; found = 84.01) was obtained in 49% yield based on the amount of trimethylallyloxysilane employed. In the case of n = 2, the product V (bp = 84 C/1.5 mm Hg; n_D^{20} = 1.4628, molar refraction calculated = 105.48; found = 106.23) was obtained in 54% yield.

Preparation of $(CH_3)_3Si\left(Si(CH_3)_2\right)_n(CH_2)_3OH$ (V") (n = 1,2). A solution mixture of water and dioxane weakly acidified with hydrochloric acid was added to V' in equivalent volume. The reaction mixture was stirred vigorously at room temperature for 20 min, and then the hexamethyldisiloxane generated in the hydrolysis, dioxane and water were removed by distillation under reduced pressure. After removing almost all of the water, benzene was added and remaining water was azeotropically removed.

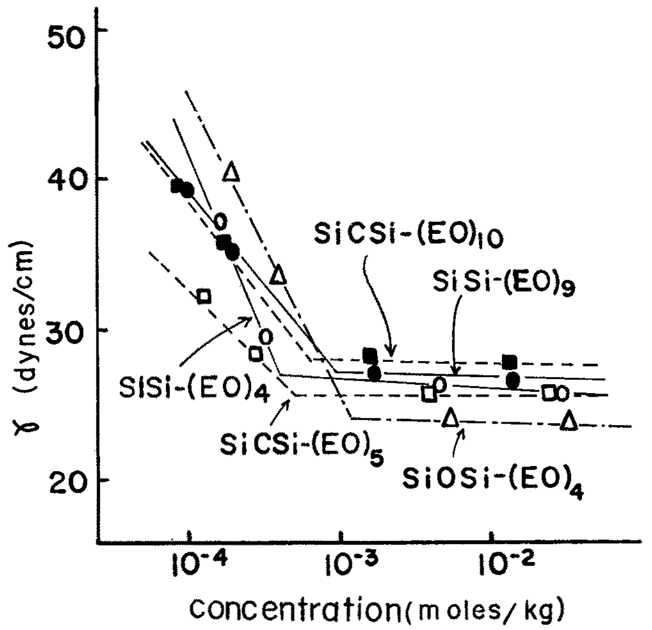


FIG. 1. Surface tension vs. concentration for nonionic surfactants containing two silicon atoms.

The product V" was quantitatively obtained. Analysis: Calculated for $C_8H_{22}Si_2O$; C, 50.99; H, 10.72. Found: C, 50.58; H, 10.98. Molecular weight calculated = 190.4; found = 192.4. Calculated for $C_{10}H_{28}Si_3O$; C, 48.51; H, 10.99. Found: C, 48.65; H, 11.10. Molecular weight calculated = 247.6; found = 248.9.

Preparation of Ethylene Oxide Adducts (V). Ethylene oxide was conducted into V" in the presence of 0.1 wt % $BF_3 \cdot Et_2O$ as the catalyst at 110 C. Such basic catalysts as CH_3ONa, NaOH and tertiary amines could not be used because of their cleaving effect on the SiSi bond. The number of oxyethylene units was determined by the increasing weight of the reaction mixture and hydroxyl value of the reaction product. They showed a good agreement.

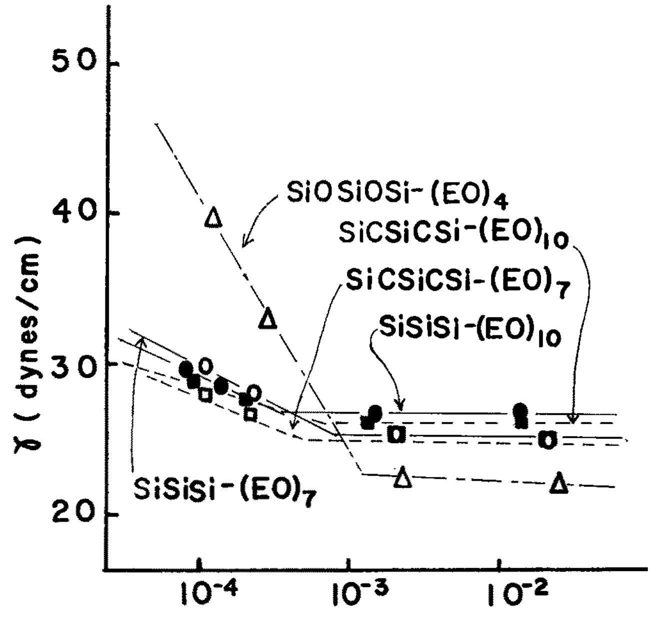


FIG. 2. Surface tension vs. concentration for nonionic surfactants containing three silicon atoms.

Syntheses of Dimethylpolysilmethylene Surfactants (VI)

Preparation of $(CH_3)_3Si\left(CH_2Si(CH_3)_2\right)_n(CH_2)_3OSi(CH_3)_3$ (VI'). ω-Hydrodisilmethylene and ω-hydrotrisilmethylene were prepared from trimethylchlorosilane by the method previously reported (4).

In a four-necked flask were placed 0.1 mole of polysilmethylene, 0.13 mole of trimethylallyloxysilane and 10 mg of $H_2PtCl_6 \cdot 6H_2O$ as the catalyst. The reaction mixture was stirred for 3 hr at 100 to 150 C, and the product fractionally distilled under reduced pressure.

In the case of n = 1, the product VI' (bp = 100 C/10 mm Hg, n_D^{20} = 1.4450) was obtained in 72% yield. Molar refraction calculated for $(CH_3)_3SiCH_2Si(CH_3)_2(CH_2)_3OSi(CH_3)_3$ = 87.48; found = 88.01. In the case of n = 2, the product VI' (bp = 116~117 C/3 mm Hg n_D^{20} = 1.4469) was obtained in 70% yield. Molar refraction calcd. for $(CH_3)_3Si\left(CH_2Si(CH_3)_2\right)_2(CH_2)_3OSi(CH_3)_3$ = 110.1; found = 110.1.

Preparation of $(CH_3)_3Si\left(CH_2Si(CH_3)_2\right)_n(CH_2)_3OH$ (VI") (n = 1,2). In analogy with polysilanes, VI' was treated with water, and polysilmethylene alcohol VI" was obtained. The product was distilled under reduced pressure. n = 1, bp = 93 C/4 mm Hg. OH value calculated = 277.0; found = 275.1. Si % calculated = 27.47; found = 27.21. n = 2, bp = 110 C/1 mm Hg. OH value calculated = 202.8; found = 199.3. Si % calculated = 30.46; found = 30.09.

Preparation of Ethylene Oxide Adducts (VI). The addition of ethylene oxide was carried out as in the case of polysilane alcohol, except for the use of KOH as the catalyst and the reaction temperature of 150 C.

Syntheses of the Dimethylpolysiloxane Nonionic Surfactants (VII)

Preparation of $CH_2=CHCH_2O(CH_2CH_2O)_mSi(CH_3)_3$ (VII"). Allylalcohol plus KOH as the catalyst were placed in a four-necked flask. Ethylene oxide was allowed to bubble into the flask by stirring under reflux of allylalcohol. When the reaction temperature rose to 148 C from 95 C, the bubbling of ethylene oxide was stopped. The reaction mixture was then fractionally distilled under reduced pressure to give two pure products with bp of 130 C/3 mm Hg and 147 C/2 mm Hg respectively. From measurements of OH values, these were confirmed to be 3 mole and 4 mole adducts of ethylene oxide to allylalcohol.

A mixture of 0.2 mole of the ethoxylated alcohol, 0.15 mole of hexamethyldisilazane and 50 ml benzene as solvent was placed in a 200 ml four-necked flask and heated for 2 hr with stirring under reflux. The reaction mixture was fractionally distilled under reduced pressure to give two products with bp 114 C/3 mm Hg and 136 C/2 mm Hg respectively. By measurement of IV these products were confirmed to be the sillylethers of the 3 mole adduct and the 4 mole adduct of ethylene oxide.

Preparation of $(CH_3)_3Si\left(OSi(CH_3)_2\right)_n(CH_2)_3O(CH_2CH_2O)_mH$ (VII). A mixture of 1.3 mole of $(CH_3)_3Si\left(OSi(CH_3)_2\right)_nH$ (n = 1,2) (6), 1 mole of VII" and 10 mg of $H_2PtCl_6 \cdot 6H_2O$ as the catalyst stirred and heated at 150 C for 3 hr in a 50 ml four-necked flask. The products were isolated by silica gel column chromatography (acetone-chloroform, (1:2), were used as eluting solvent). After removing

TABLE I
Fractionation of SiSiSi–$(EO)_{8.4}$ by Column Chromatography

Fraction	Molecular weight	Number of oxyethylene units (mole)
1	562.2	7.1
2	597.8	8.0
3	733.7	11.1
Average	631.2	8.4

unreacted material under reduced pressure, the product was obtained in 82–87% yield.

These silylethers containing polysiloxane group were treated with a mixture of water and dioxane weakly acidified with hydrochloric acid as in the case of V'.

OH value calculated for $(CH_3)_3SiOSi(CH_3)_2(CH_2)_3O(CH_2CH_2O)_3H$ = 165.6; found = 168. Si % calculated = 16.59; found = 16.86. OH value calculated for $(CH_3)_3Si\left(OSi(CH_3)_2\right)_2(CH_2)_3O(CH_2CH_2O)_4H$ = 122.8; found = 125. Si % calculated = 18.44; found = 18.01.

Results and Discussion

For convenience the following abbreviations are used to designate the structural formulas of silicone surfactants.

$(CH_3)_3SiSi(CH_3)_2(CH_2)_3O(CH_2CH_2O)_mH$ = SiSi–$(EO)_m$
$(CH_3)_3SiCH_2Si(CH_3)_2$ = SiCSi, $(CH_3)_3SiOSi(CH_3)_2$ = SiOSi

With regard to surfactants containing three silicon atoms, similar abbreviations are also used.

Aqueous Surface Tensions

Surface tension was measured with a du Noüy tensiometer. The results from surfactants containing two silicon atoms and those containing three silicon atoms are shown in Figures 1 and 2, respectively. In the concentration above critical micelle concentration, polysilane and polysilmethylene surfactants reduce the surface tension as low as 25 to 26 dynes/cm in an aqueous solution, while polysiloxane surfactants cause a reduction from 21 to 22 dynes/cm, thus being the most efficient.

In the case of polysilane surfactants, $BF_3 \cdot Et_2O$ was used as the catalyst in the preparation of the ethylene oxide adducts. It is therefore to be expected that the molecular weight distribution of the products is broad. As shown in Table I, the polysilane surfactants obtained were fractionated into three sections by silica gel column chromatography (acetone being used as eluting solvent). The results of the measurement of the surface tension of these three fractions are shown in Figure 3. Above the critical micelle concentration, these results show that the surface tensions of these fractions are nearly equal to those of starting polysilane surfactants.

Interfacial Tension Between Water and Silicone Oil

Interfacial tension between water and silicone oil (dimethylpolysiloxane d_4^{25} = 0.9332) was measured by du Noüy's ring method. The results are shown in Figure 4. Polysilmethylene is most effective in aqueous solution below 0.5 wt %. Above this concentration, however, polysiloxane surfactants are the most effective of three. The data on ethylene oxide 7.4 mole adducts to lauryl alcohol are included for comparison in Figure 4.

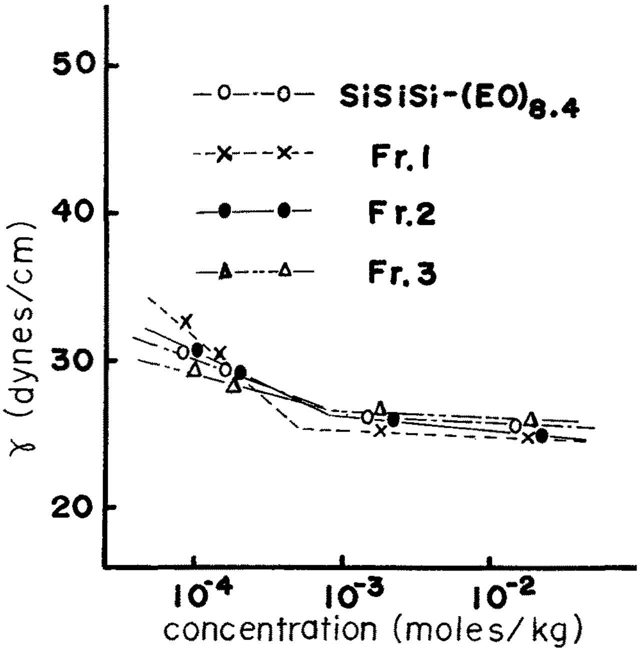


FIG. 3. Surface tension vs. concentration for SiSiSi-$(EO)_{8.4}$.

Surface Tension of Polyethylene Glycol

As an example of the surface tension lowering ability in a nonaqueous solution, that of polyethylene glycol (p = 200) was measured by du Noüy's ring method in 1.0 wt % polyethylene glycol solution. The data in Table II demonstrates that there is no difference among surfactants containing two silicon atoms, while polysiloxane surfactants are the most effective in lowering the surface tension of the polyol among surfactants containing three silicon atoms.

Wetting Ability

The spreading of a liquid on a solid is determined by the spreading coefficient:

$$S = r_s - (r_l + r_{s/l})$$

A liquid will wet out a solid if the spreading coefficient is positive. Low liquid surface tensions promote spreading, while materials which have low surface energies are correspondingly more difficult to wet (7).

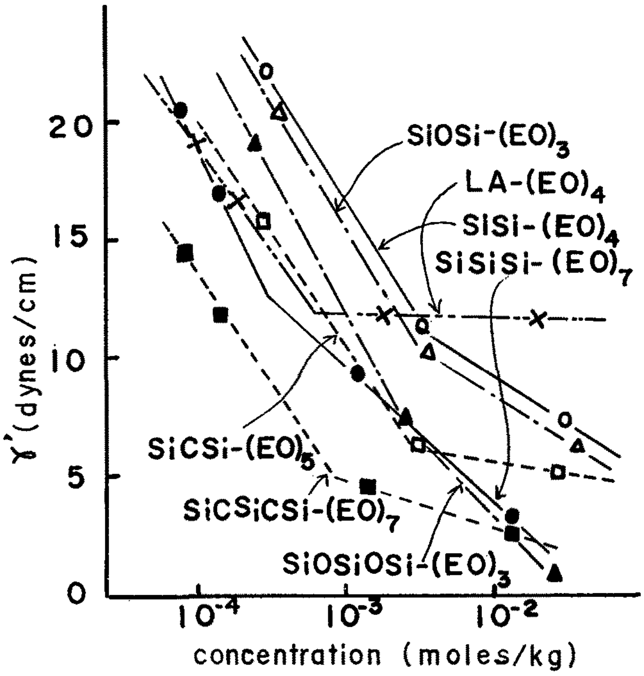


FIG. 4. Interfacial tension between water and silicon oil (d^{25} = 0.9332) vs. concentration.

TABLE II

Surface Tension of Polyethylene Glycol ($p = 200$, 1.0 wt % solution, 25 C), Wetting Ability to Polyethylene and Cloud Point

Surfactant	Surface tension (dyne/cm)	Wetting ability, % (1.0 wt % solution, 25 C)	Cloud point, C (0.1 wt % solution)
None	47.6	100	......
SiSi–$(EO)_4$	38.9	>300	18.5
SiSi–$(EO)_9$	38.9	260	49.0
SiSiSi–$(EO)_7$	33.0	280	29.0
SiSiSi–$(EO)_{10}$	32.8	200	41.5
SiCSi–$(EO)_5$	38.3	200	79.0
SiCSi–$(EO)_{10}$	38.3	180	81.5
SiCSiCSi–$(EO)_7$	35.6	220	70.0
SiCSiCSi–$(EO)_{10}$	35.0	190	76.0
SiOSi–$(EO)_3$	38.1	190	< 0
SiOSiOSi–$(EO)_4$	23.8	>300	< 0
Lauryl alcohol–$(EO)_{7.4}$	42.9	140	54.0

The wetting ability on polyethylene was measured in the following way.

On a clear polyethylene sheet, aqueous solution of surfactants 0.02 ml of pure water and 0.1 wt % were respectively placed. The diameters of water and sample solution drops, R_0 and R respectively, were measured after 3 min. Wetting ability W was calculated from the following equation.

$$W = R/R_0 \times 100\ (\%)$$

The results are shown in Table II. Some of polysilane and polysiloxane surfactant solutions rapidly spread to thin film (wet out) on low energy hydrophobic surfaces such as polyethylene.

Cloud Point

The cloud points of 0.1 wt % solutions were measured by the usual method. The results are shown also in Table II.

REFERENCES

1. Kanner, B., W. G. Reid and I. H. Petersen, Ind. Eng. Chem. Prod. Res. Develop. *6*, 88 (1967).
2. Maki, H., M. Komatsu and S. Komori, Kogyo Kagaku Zasshi *70*, 1771 (1967).
3. Maki, H., Y. Murakami, I. Ikeda and S. Komori, Ibid. *71*, 1675 (1968).
4. Maki, H., Y. Murakami, I. Ikeda and S. Komori, Ibid. *71*, 1679 (1968).
5. Kumada, T., M. Ishikawa and S. Maeda, J. Organometal. Chem. *2*, 478 (1964).
6. Greber, G., and L. Metzinger, Makromol Chem. *39*, 189 (1960).
7. Schwarg, E. G., and W. G. Reid, Ind. Eng. Chem. *56*, 26 (1964).

[Received June 3, 1969]