Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

SYNTHESIS AND AGGREGATION BEHAVIOR OF OLEFINIC QUATERNARY AMINO SILOXANES

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To cite this Article Vaidya, Ashish A. and Kumar, V. G.(1999) 'SYNTHESIS AND AGGREGATION BEHAVIOR OF OLEFINIC QUATERNARY AMINO SILOXANES', Journal of Macromolecular Science, Part A, 36: 4, 587 — 603
To link to this Article: DOI: 10.1081/MA-100101550
URL: http://dx.doi.org/10.1081/MA-100101550

J.M.S.—PURE APPL. CHEM., A36(4), pp. 587–603 (1999)

SYNTHESIS AND AGGREGATION BEHAVIOR OF OLEFINIC QUATERNARY AMINO SILOXANES

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Key Words: Synthesis, Olefinic Quaternary Amino Siloxane, Aggregation

ABSTRACT

Monomeric and oligomeric siloxanes with quaternary amine and olefinic substitutions were synthesized by a reaction scheme involving hydrosilation of Si-H containing siloxanes (monomeric as well as oligomeric) with allyl glycidyl ether in the presence of hexachloroplatinic acid followed by reaction with allyl amine. Olefinic amino hydroxysiloxanes thus obtained were quaternized using methyl iodide. The above mentioned products were found to be highly surface active as was indicated by surface tension measurements. The lowering in surface tension was found to depend upon the number of siloxane units. The aggregation behavior was studied using ^{1}H-NMR in D_2O, DMSO-d_6 and acetone-d_6.

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INTRODUCTION

Quaternary amine derivatives of siloxanes have been reported to have surface active properties and excellent binding to primarily negatively charged substrates like hair and fabrics. They find application as emulsifier [1], hair and skin conditioning agents [2], textile softeners [3] etc. Siloxane chains are known to have high flexibility due to the easy rotation of Si-O-Si and Si-C bonds resulting in improved film forming properties at the air-water interface. In comparison, the -$(CH_2)_n$- moiety in the surfactants having hydrocarbon chain have higher surface energy [4] as compared to dimethyl groups on siloxane backbone [5]. Thus introduction of siloxane moiety can be expected to improve the surface-active properties of surfactants having hydrocarbon chain as hydrophobic segment.

Synthetic procedures for quaternary siloxanes describe

(1) reaction of epoxy [6, 3] or halogenated siloxane [7-10] with amines followed by quaternization,

2) reaction of carboxylic acid functional quaternary ammonium compounds with amino propyl trialkoxy silane or siloxanes compounds [11] and

3) hydrosilation of alkenyl amine in the presence of platinum catalyst followed by quaternization. J. Martisons synthesized and characterized non ionic and cationic aminohydroxy functional siloxanes [3] by reacting Si-H containing molecules (having formula $Me_3SiO(SiMe_2O)_x$ $(SiMeHO)_ySiMe_3$, where, (1) x=0, y=1; (2) x=0, y=33 and (3) x=150, y=23) with allyl glycidyl ether followed by reaction with hexylamine, benzyl amine, dicyclohexyl amine or methyl amine. The amino hydroxy siloxanes obtained were quaternized using HBr to give cationic siloxane.

Our objective is to synthesize monomeric and oligomeric siloxanes with quaternary amine and olefinic substitutions. The olefinic end groups were introduced with an objective of synthesizing block/graft copolymers by functionalizing the double bonds (eg. epoxidation) and reaction with dicarboxylic macromers and their presence served as excellent markers for the ^{1}H-NMR studies on aggregation behavior. These olefinic quaternary amino siloxanes were synthesized by a reaction scheme involving hydrosilation of Si-H containing siloxanes (monomeric as well as oligomeric) with allyl glycidyl ether in the presence of platinum catalyst followed by reaction with allyl amine. Olefinic amino hydroxy siloxanes thus obtained were quaternized using methyl iodide. The above mentioned products were found to be highly surface active as was indicated by surface tension measurements. The aggregation behavior was studied using ^{1}H-NMR in D_2O, DMSO-d_6 and acetone-d_6.

EXPERIMENTAL

Methods

FTIR analysis was carried out using BOMEN FTIR spectrophotometer. NMR spectra were recorded on Bruker ACP 200 spectrometer (200MHz) using $CDCl_3$, D_2O as a solvent. Chemical shifts of various peaks in the spectra were reference with respect to HDO peak appearing at 4.78 ppm in D_2O, $CHCl_3$ peak appearing at 7.26 in $CDCl_3$ and tetramethylsilane at 0 ppm in acetone-d_6 and dimethyl sulfoxide-d_6. The surface tension measurements were carried out using Kruss tensiometer K10, at 25° C. Aggregation studies on quaternary amino siloxanes were carried out in D_2O, DMSO-d_6 and CD_3-CO-CD_3. The spectra were recorded under identical conditions in a concentration range 0.06 to 33.19 mM and 2.12 to 33.73 mM for monomeric and oligomeric quaternary amino siloxanes respectively.

Chemicals

Dimethyl dichlorosilane (98%, Spectrochem); methyldichloro silane (98%, Fluka); chlorodimethyl silane (96%, Fluka); allyl glycidyl ether (97%, Lancaster); hexachloroplatinic acid i.e. $H_2PtCl_6.6H_2O$, (Fisher Scientific company, New Jersey); allyl amine (98%, Lancaster); methyliodide (99%, SISCO Research Lab.); butyl lithium (1.6 M solution in hexane, Fluka); THF (dried over sodium); toluene (dried over sodium).

Experimental Procedures

Diepoxy tetramethyldisiloxane and multifunctional epoxy polysiloxanes were obtained by hydrosilation of tetramethyl disiloxane and Si-H containing linear polysiloxanes respectively in the presence of a hexachloroplatinic acid catalyst. The epoxy groups were opened up by reaction with allylamine to give olefinic aminohydroxy siloxanes. Quaternization of amino group using methyl iodide gave water-soluble siloxanes. The CMC's were determined by surface tension measurements.

(a) Synthesis of Tetramethyl Disiloxane (A1)

150 g (1.57 moles) of chlorodimethyl silane was added dropwise to 200 mL water in a 500 mL two-necked round bottom flask at 10°C. The mixture was stirred for 2 hours at 20°C. The acidic aqueous layer (residual HCl)

was then separated and the organic layer was washed with distilled water till neutral pH. Tetramethyl disiloxane thus obtained was dried over anhydrous sodium sulfate and characterized by FTIR, ^{1}H-NMR.

Siloxane (A1): Clear transparent liquid, 81% yield, FTIR resonance frequency due to Si-H at 2159 cm^{-1}, Si-CH^3 at 1260 cm^{-1}, -Si-O-Si- at 1050-1100 cm^{-1}; ^{1}H-NMR peaks at δ (ppm) 0.17 (Si-C**H**$_3$, s), 4.67 (Si-**H**, s).

(b) Synthesis of Si-H Containing Cyclic Siloxane (A2)

150 mL of water and 150 mL of ether were taken in a 500 mL three necked round bottom flask and then cooled to 0°C. A mixture of 129 g (1 mole) dimethyldichloro silane and 115 g (1 mole) methyldichloro silane (mole ratio 1:1) was added dropwise by maintaining the temperature at 0-5°C, during the addition. After the complete addition, the reaction mixture was stirred for 15 minutes. The acidic aqueous layer (residual HCl) was then separated and the organic layer was washed with distilled water till neutral pH. The organic layer was then dried over anhydrous sodium sulfate and the ether was evaporated off. Cyclic siloxane was distilled off under 0.1 mm vacuum at 90°C. The product was then characterized by FTIR and ^{1}H-NMR.

Siloxane (A2) Heptamethyl cyclotetrasiloxane: Clear transparent liquid, 78% yield, FTIR resonance frequency due to Si-H at 2159 cm^{-1}, Si-CH^3 1260 cm^{-1}; ^{1}H-NMR peaks at δ (ppm) 0.066 (Si (C**H**$_3$)$_2$, s), 0.13 (SiHC**H**$_3$, s), 4.68 (Si-**H**, s).

(c) Synthesis of Linear Si-H Siloxane from Cyclic Si-H Containing Siloxane (B2)

8 mL butyl lithium (0.0128 moles) was taken in a 150 mL dry round bottom flask containing 50 mL dry THF under the inert atmosphere of nitrogen. A solution of 15 g of cyclic siloxane (A2) in 40 mL of dry THF was injected dropwise into the flask containing BuLi/THF solution at -30°C and the reaction mixture was stirred for 12 hours at 0°C under the nitrogen atmosphere. The living polymer was terminated by the addition of 2.5 g (0.023 moles) trimethyl chlorosilane. The solvent and unreacted SiMe$_3$Cl were distilled off under vacuum and LiCl precipitate was filtered off. The product was then washed with water, dried under vacuum and characterized using FTIR and ^{1}H-NMR.

Siloxane (B2): Clear transparent liquid, 91% yield, FTIR resonance frequency due to Si-H at 2159 cm^{-1}, Si-CH$_3$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1}; ^{1}H-

NMR peaks at δ (ppm) 0.089 ($Si(C\underline{\mathbf{H}}_3)_2$, s), 0.171 ($SiHC\underline{\mathbf{H}}_3$, s), 0.5 ($-C\underline{\mathbf{H}}_2Si$, t), 0.86 ($-C\underline{\mathbf{H}}_3$, t), 1.57 ($-C\underline{\mathbf{H}}_2-$, m), 4.68 ($Si-\underline{\mathbf{H}}$, s).

(d) Synthesis of Epoxy Siloxane via Hydrosilation: Siloxane (B1), (C2)

11.4 g (0.1 moles) allyl glycidyl ether (AGE) was taken in two-necked round bottom flask and 1.0 mL of 3% solution of hexachloro platinic acid in IPA was added to it and the mixture was stirred at 0°C for ten minutes. Solution of 5.3 g (0.04 moles) siloxane (A1) or 18 g (0.014 moles) of (B2) in 50 mL dry toluene was added dropwise to allyl glycidyl ether-platinum mixture under inert atmosphere of nitrogen. Reaction mixture was stirred at 10°C, till disappearance of FTIR resonance frequency due to Si-H (2159 cm^{-1}). Toluene and excess AGE were distilled off under vacuum. Epoxy siloxanes (B1, C2) thus obtained were characterized by FTIR and ^{1}H-NMR.

Siloxane (B1): Clear, transparent oil, 85% yield, FTIR resonance frequency due to $Si-CH_3$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR peaks at δ (ppm) 0.1($SiC\underline{\mathbf{H}}_3$, s), 0.5 ($C\underline{\mathbf{H}}_2Si$, t), 1.57 ($-C\underline{\mathbf{H}}_2CH_2Si-$, m), 2.7 (epoxy $-C\underline{\mathbf{H}}_2$, d), 3.13 (epoxy $-C\underline{\mathbf{H}}$, m), 3.4 ($-C\underline{\mathbf{H}}_2OC\underline{\mathbf{H}}_2\ (CH_2)_2Si$, m); ^{13}C NMR peaks at δ -0.4 ($Si-\underline{\mathbf{C}}H_3$), 14 ($-\underline{\mathbf{C}}H_2Si$), 23.9 ($-\underline{\mathbf{C}}H_2CH_2Si-$), 44.6 (e-poxy $-\underline{\mathbf{C}}H_2$), 53 (epoxy $-\underline{\mathbf{C}}H$), 71, 74 ($-\underline{\mathbf{C}}H_2O\underline{\mathbf{C}}H_2(CH_2)_2Si$).

Siloxane (C2): Clear, transparent viscous oil, 88% yield, FTIR resonance frequency due to $Si-CH_3$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR peaks at δ (ppm) 0.1($SiC\underline{\mathbf{H}}_3$, s), 0.5 ($-C\underline{\mathbf{H}}_2Si$, t), 0.86 ($-C\underline{\mathbf{H}}_3$, t), 1.34 ($CH_3-C\underline{\mathbf{H}}_2-C\underline{\mathbf{H}}_2-CH_2$, m), 1.57 ($-C\underline{\mathbf{H}}_2CH_2Si-$, m), 2.7(epoxy $-C\underline{\mathbf{H}}_2$, d), 3.13 (epoxy $-C\underline{\mathbf{H}}$, m), 3.4 ($-(C\underline{\mathbf{H}}_2OC\underline{\mathbf{H}}_2\ (CH_2)_2Si$, m); ^{13}C-NMR peaks at δ-0.4 ($Si-\underline{\mathbf{C}}H_3$), 14 ($-\underline{\mathbf{C}}H_2Si$), 23.9 ($-\underline{\mathbf{C}}H_2CH_2Si-$), 44.6 (epoxy $-\underline{\mathbf{C}}H_2$), 53 (epoxy $-\underline{\mathbf{C}}H$), 71, 74 ($-\underline{\mathbf{C}}H_2O\underline{\mathbf{C}}H_2(CH_2)_2Si$).

(e) Synthesis of Olefinic Aminohydroxy Siloxanes: (C1), (D2)

A solution of 18 g of epoxy siloxane [0.05 moles of B1 or 0.01 moles of C2] in 35 mL dry toluene was taken in a dry three-necked round bottom flask attached with a reflux condenser. 15 g (0.25 moles) allyl amine was added to it and the reaction mixture was refluxed at 100°C for 7 hours under the nitrogen atmosphere. Excess allylamine and toluene were distilled off and the light yellow product (siloxane (C1), (D2)) was characterized by FTIR, ^{1}H and ^{13}C-NMR.

Siloxane (C1): Clear, pale yellow transparent oil, 96% yield, FTIR resonance frequency due to CH-OH and –NH (broad hump) at 3407 cm^{-1}, $Si-CH_3$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR peaks at δ (ppm)

0.1($\mathrm{SiC}\underline{\mathbf{H}}_3$, s), 0.5 ($\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{Si}$, t), 1.57 ($\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{-CH_2Si-}$, m), 2.58 ($\mathrm{CH(OH)-C}\underline{\mathbf{H}}_2\mathrm{-NH}$ and $\mathrm{CH_2{=}CH-C}\underline{\mathbf{H}}_2\mathrm{NH}$, overlapped doublets), 3.85 ($\mathrm{-C}\underline{\mathbf{H}}$ (OH), m), 5.17 ($\mathrm{C}\underline{\mathbf{H}}_2\mathrm{{=}CH}$, m), 5.7 ($\mathrm{-C}\underline{\mathbf{H}}\mathrm{{=}CH_2}$, t); ^{13}C NMR peaks at δ -0.4 ($\mathrm{Si-}\underline{\mathbf{C}}\mathrm{H_3}$), 14 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2Si}$), 23.9 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2CH_2Si-}$), 68.06 ($\mathrm{NH-}\underline{\mathbf{C}}\mathrm{H_2-CH{=}CH_2}$), 70,74 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2O}\underline{\mathbf{C}}\mathrm{H_2\ (CH_2)_2Si}$), 125-130 ($\mathrm{CH_2-}\underline{\mathbf{C}}{=}\underline{\mathbf{C}}$).

Siloxane (D2): Clear, pale yellow viscous oil, 95% yield, FTIR resonance frequency due to CH-OH and –NH at 3407 cm^{-1} (broad hump) $\mathrm{Si-CH_3}$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR peaks at δ (ppm) 0.1($\mathrm{SiC}\underline{\mathbf{H}}_3$, s), 0.5 ($\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{Si}$, t), 0.86 ($\mathrm{-C}\underline{\mathbf{H}}_3$, t), 1.34 ($\mathrm{CH_3-C}\underline{\mathbf{H}}_2\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{-CH_2}$, m), 1.57 ($\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{CH_2Si-}$, m), 2.58 ($\mathrm{CH\ (OH)-C}\underline{\mathbf{H}}_2\mathrm{-NH}$ and $\mathrm{CH_2{=}CHC}\underline{\mathbf{H}}_2\mathrm{\ NH}$, overlapped doublets), 3.85($\mathrm{-C}\underline{\mathbf{H}}$ (OH), m), 5.17 ($\mathrm{C}\underline{\mathbf{H}}_2\mathrm{{=}CH}$, m), 5.7 ($\mathrm{-C}\underline{\mathbf{H}}\mathrm{{=}CH_2}$, m); ^{13}C-NMR peaks at δ -0.4 ($\mathrm{Si-}\underline{\mathbf{C}}\mathrm{H_3}$), 14 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2Si}$), 23.9 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2CH_2Si-}$), 68.06 ($\mathrm{NH-}\underline{\mathbf{C}}\mathrm{H_2-CH{=}CH_2}$), 52 ($\mathrm{CH\ (OH)\ }\underline{\mathbf{C}}\mathrm{H_2-NH}$), 70,74.5 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2O}\underline{\mathbf{C}}\mathrm{H_2\ (CH_2)_2Si}$), 125-130 ($\mathrm{CH_2-}\underline{\mathbf{C}}{=}\underline{\mathbf{C}}$)

(f) Synthesis of Quaternary Amino Siloxane: Siloxane (D1), (E2)

5 g of siloxane (0.01 moles of C1 or 0.0023 moles of D2) in 30 mL toluene was taken in two-necked dry round bottom flask and 10 g (0.07 moles) of methyl iodide was added. The reaction mixture was stirred at 60°C for 5 hours and then allowed to settle at room temperature for 4-5 hours. The quaternary amino siloxane (D1) or (E2) separated was washed with toluene and characterized by FTIR, ^{1}H and ^{13}C-NMR.

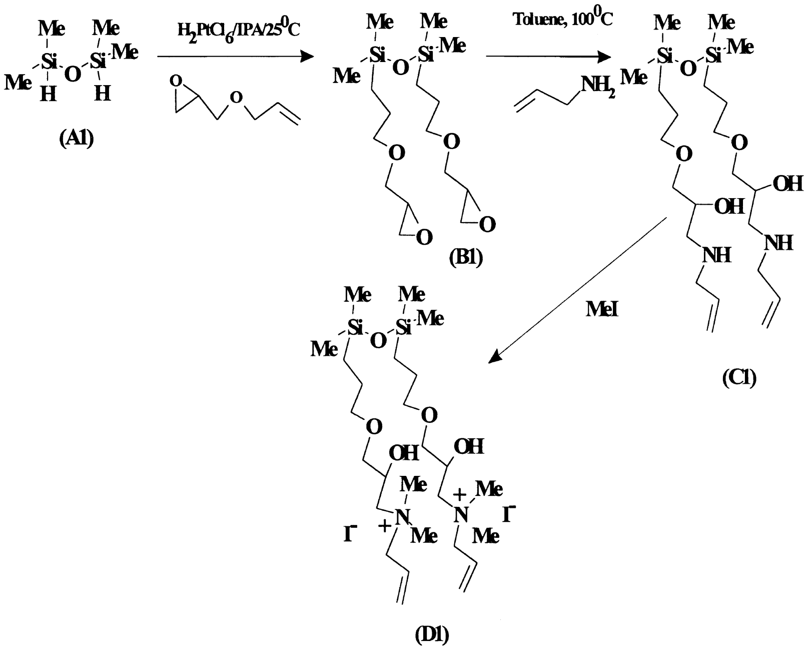
Siloxane (D1): Clear, amber colored transparent oil, 96% yield, FTIR resonance frequency due to CH-OH at 3407 cm^{-1}, $\mathrm{Si-CH_3}$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR peak at δ (ppm) 0.1($\mathrm{SiC}\underline{\mathbf{H}}_3$, s), 0.5 ($\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{Si}$, t), 1.57 ($\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{CH_2Si-}$, m), 3.3 ($\mathrm{Si(CH_2)_2C}\underline{\mathbf{H}}_2\mathrm{OC}\underline{\mathbf{H}}_2\mathrm{-}$, m), 4.5 ($\mathrm{-N^+-C}\underline{\mathbf{H}}_2\mathrm{-C{=}C-}$, m), 5.17 ($\mathrm{C}\underline{\mathbf{H}}_2\mathrm{{=}CH}$, m), 5.7 ($\mathrm{-C}\underline{\mathbf{H}}\mathrm{{=}CH_2}$, m); ^{13}C-NMR peaks at δ -0.4 ($\mathrm{Si-}\underline{\mathbf{C}}\mathrm{H_3}$), 14 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2Si}$), 23.9 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2CH_2Si-}$), 54 ($\mathrm{C}\underline{\mathbf{H}}\mathrm{(OH)}$), 65 ($\mathrm{-N^+-}\underline{\mathbf{C}}\mathrm{H_2-C{=}C}$), 70,74.5 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2O}\underline{\mathbf{C}}\mathrm{H_2(CH_2)_2Si}$), 125-130 ($\mathrm{CH_2-}\underline{\mathbf{C}}{=}\underline{\mathbf{C}}$).

Siloxane (E2): Clear, amber colored, viscous oil, 92% yield, FTIR resonance frequency due to CH-OH at 3407 cm^{-1}, $\mathrm{Si-CH_3}$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR peak at δ (ppm) 0.1($\mathrm{SiC}\underline{\mathbf{H}}_3$, s), 0.5 ($\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{Si}$, broad singlet), 0.86 ($\mathrm{-C}\underline{\mathbf{H}}_3$, t), 1.34 ($\mathrm{CH_3-C}\underline{\mathbf{H}}_2\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{-CH_2}$, m), 1.57 ($\mathrm{-C}\underline{\mathbf{H}}_2\mathrm{CH_2\ Si-}$, m), 3.3 ($\mathrm{Si\ (CH_2)_2C}\underline{\mathbf{H}}_2\mathrm{OC}\underline{\mathbf{H}}_2\mathrm{-}$, m), 4.5 ($\mathrm{-N^+-C}\underline{\mathbf{H}}_2\mathrm{-C{=}C-}$), m), 5.17 ($\mathrm{C}\underline{\mathbf{H}}_2\mathrm{{=}CH}$, m), 5.7 ($\mathrm{-C}\underline{\mathbf{H}}\mathrm{{=}CH_2}$, m); ^{13}C-NMR peaks at δ -0.4 ($\mathrm{Si-}\underline{\mathbf{C}}\mathrm{H_3}$), 14 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2Si}$), 23.9 ($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2CH_2Si-}$), 54 ($\mathrm{C}\underline{\mathbf{H}}\mathrm{(OH)}$), 65 ($\mathrm{-N^+-}\underline{\mathbf{C}}\mathrm{H_2-C{=}C}$), 70,74.5($\mathrm{-}\underline{\mathbf{C}}\mathrm{H_2O}\underline{\mathbf{C}}\mathrm{H_2(CH_2)_2Si}$), 125-130 ($\mathrm{CH_2-}\underline{\mathbf{C}}{=}\underline{\mathbf{C}}$).

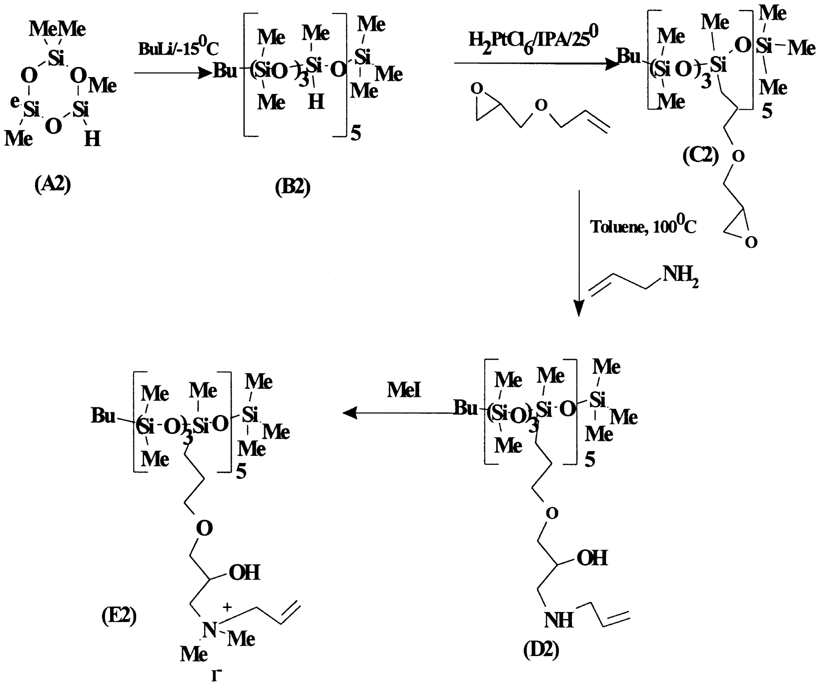
RESULTS AND DISCUSSION

Synthesis of Quaternary Amino Siloxane

Two different types of approaches (Schemes 1 and 2) were adopted to synthesize quaternary amino siloxanes. Scheme 1 gave monomeric quaternary amino siloxane, while Scheme 2 gave oligomeric quaternary amino siloxane. As indicated in Scheme 1, tetramethyl disiloxane (A1) was converted to epoxy siloxane by reaction with allyl glycidyl ether in the presence of hexachloroplatinic acid. This was followed by reaction with allyl amine and quaternization using methyl iodide to give monomeric quaternary amino siloxane (D1). Quaternary amino siloxane (D1) was dissolved in water, and the aqueous layer was washed with toluene to remove organic impurities. The structure and ^{1}H-NMR spectra in acetone are shown in Figure 1A. In Figure 1A, the peak is due to a small amount of moisture, at δ (ppm) 3.01 appears during the solvent suppression of peak due to acetone-d at δ (ppm) 2.1, and the peak at δ (ppm) 1.2 is due to minute amounts of impurity $((CH_3)_2Si\text{-}O\text{-}CH(C\underline{\mathbf{H}}_3)_2)$ left which were formed due to a side reaction of IPA with few Si-H groups during hydrosilation reaction (% impurity = 1-2).

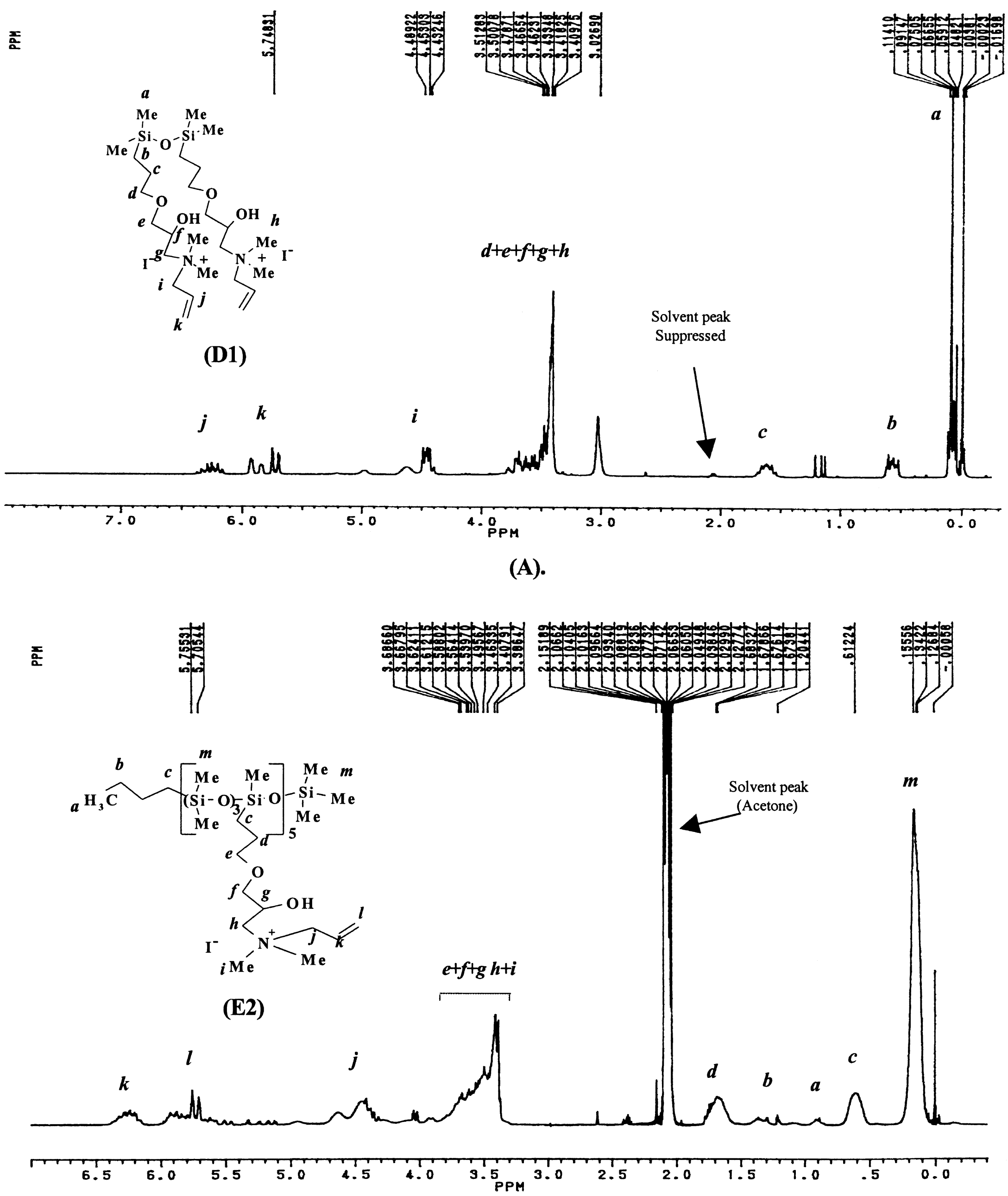


Scheme 1. Synthesis of monomeric quaternary amino siloxane.



Scheme 2. Synthesis of oligomeric quaternary amino siloxane.

Co-hydrolysis of dichlorodimethyl silane and methyl dichloro silane gave a mixture of cyclic siloxane and high molecular weight polymer. Cyclic siloxane (A2) was distilled off under 0.1 mm vacuum at 90°C and characterized by ^{1}H-NMR. In Scheme 2, cyclic siloxane (A2) on ring opening polymerization using butyl lithium (1.6 M solution in n-hexane) gave a living polymer which was terminated by the addition of trimethyl chloro silane to give Si-H containing oligomer (B2). The oligomer contains butyl group at one end and trimethyl silyl group at the other end. (^{1}H-NMR showed the presence of $-Si(C\underline{\mathbf{H}}_3)_2$, $-Si\underline{\mathbf{Me}}H$, $-C\underline{\mathbf{H}}_2Si$, $C\underline{\mathbf{H}}_3-$, $-C\underline{\mathbf{H}}_2-$, $Si-\underline{\mathbf{H}}$ groups at δ 0.06, 0.12, 0.54, 0.86, 1.35, 4.65 respectively). Control in the molecular weight was achieved by varying the butyl lithium concentration. The Si-H containing oligomers thus obtained were converted into epoxy siloxane oligomers (C2) by hydrosilation with allyl glycidyl ether in the presence of $H_2PtCl_6.6H_2O$ (3% solution in IPA). Toluene and excess allyl glycidyl ether were distilled off under vacuum. The epoxy siloxane oligomers were characterized by ^{1}H and ^{13}C-NMR spectroscopy. The ^{1}H-NMR peaks (and integration area) due to epoxy CH and epoxy CH_2 shows the absence of crosslinking



(A).

(B).

Figure 1. ^{1}H-NMR of A) Monomeric quaternary siloxane in acetone. Peak at d (ppm) 3.02 is due to moisture in the sample after solvent suppression. B) Oligomeric quaternary siloxane in acetone-d (peak due to TMS and acetone at d (ppm) 0 and 2.07.

due to epoxy ring opening in the presence of platinum catalyst. Allylamine on reaction with epoxy siloxanes (C2) gave olefinic aminohydroxy siloxanes (D2) (^{1}H-NMR showed the presence of $-CH_2-NH-C\underline{\mathbf{H}}_2CH$ (OH) and $-C\underline{\mathbf{H}}=C\underline{\mathbf{H}}_2$ at (2.5-2.7 and 5.2-5.7, respectively) which on quaternization using methyl iodide gave oligomeric quaternary amino siloxanes (E2). The structure and ^{1}H-NMR spectra in acetone-d are shown in Figure 1B.

Determination of Surface Activity

The surface active properties of the above mentioned olefinic quaternary amino siloxanes were studied by surface tension measurements and it was found that a lowering in surface tension by oligomeric quaternary siloxane (22 mN/m) was more than that observed for monomeric quaternary siloxane (24 mN/m). The results are given in Figure 2. The surface tension at various concentrations were compared with linear alkyl benzene sulfonate (LAS, hydrocarbon surfactant).

The drastic changes in the slope of surface tension v/s log concentration of surfactants is generally interpreted to be due to surfactant aggregation into micelle [12]. But minor discontinuity in slope can be explained as a result of aggregation not resulting in micellisation. Based on these results, it can be interpreted that monomeric quaternary amino siloxanes associate at low concentration and form micelle at 7 mM. Oligomeric quaternary aminosiloxanes, on the

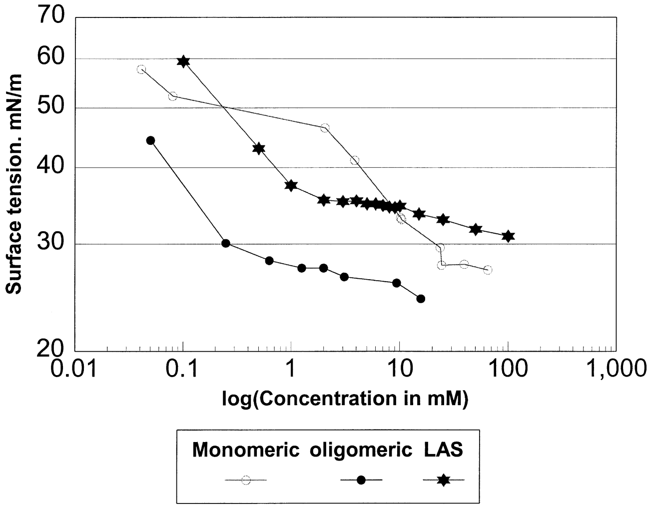


Figure 2. Plot of surface tension v/s log concentration for monomeric and oligomeric quaternary amino siloxane.

other hand, do not appear to form micelle. They, in fact, show lower surface tension even at very low concentrations and the aggregation occurs at a concentration of 0.6 mM. The high molecular weight and flexibility of -Si-O-Si- backbone is explained as a result of linear spreading of siloxane molecule at air/water interface resulting in low surface tension.

Aggregation Study of Quaternary Amino Siloxane at Different Solvents—^{1}H-NMR Results

The aggregation behavior and micelle structure of Linear alkyl benzene sulfonate was investigated by a variety of techniques such as NMR [13, 14] and fluorescence spectroscopy [15]. Aggregation was shown to be dependent on the dielectric constant of the medium. In the case of polar solvent, surfactant forms micelles which have a non polar core. In contrast, when the solvent is non polar, reverse micelle with a polar core is formed. Aggregation of quaternary amino siloxane (D1) at varying concentrations (above and below CMC) was studied in D_2O, DMSO-d_6 and CD_3COCD_3 having dielectric constants 78, 48 and 20 respectively using ^{1}H-NMR. The chemical shifts of $-N^+(C\mathbf{H}_3)_2$, $-N^+-C\underline{\mathbf{H}}_2-CH=CH_2$, $-CH=C\underline{\mathbf{H}}_2$ and $-C\underline{\mathbf{H}}=CH_2$ in the siloxane (D1) were monitored at concentrations above and below CMC. The results are given in Table 1.

From Table 1, it can be observed that in the case of D_2O, DMSO-d_6, and acetone-d_6 there were no changes in the chemical shifts of $-N^+(C\mathbf{H}_3)_2$, $-CH=C\underline{\mathbf{H}}_2$, $-C\underline{\mathbf{H}}=CH_2$ due to increase in the concentration from 0.06 to 33.19 mM. In D_2O there was no shift for the proton flanked between quaternary nitrogen and C=C (i.e. $-N^+-C\underline{\mathbf{H}}_2-CH=CH_2$). However, for the same proton a downfield shift was observed in acetone and DMSO when concentrations were varied from below CMC to above CMC (Figures 3 and 4).

These results can be explained as follows. In water, groups attached to quaternary nitrogen are present in the palisade layer (i.e. layer between organic core and aqueous layer) Figure 5A, due to the fact that there was no change in environment of protons and the chemical shifts remained the same, at all the concentrations. In the case of DMSO, the $-N^+-C\underline{\mathbf{H}}_2-CH=CH_2$ groups penetrated the palisade layer and entered in the organic core containing C-O-C and Si-O-Si linkages (Figure 5B) leading to the change in environment around that proton. As the dielectric constant decreases the width of palisade layer decreases and thereby penetration of $-N^+-C\underline{\mathbf{H}}_2-CH=CH_2$ increases into the palisade layer which is more in the case of the acetone as compared to DMSO and D_2O. The possible models for micelli in water and DMSO or acetone are proposed in Figure 5.

TABLE 1. Variation in ^{1}H-NMR Chemical Shifts of Monomeric Quaternary Amino Siloxane (D1) at Varying Concentrations in D_2O, CD_3, and d_6 DMSO

Conc. (mM)	**$-N^+-C\underline{H}_2-CH=CH_2$**			**$-CH(OH)C\underline{H}_2-N^+-$ and $-N^+(C\underline{H}_3)_2$**			**$-C\underline{H}=CH_2$ and $-CH=C\underline{H}_2$**		
	D_2O	**DMSO (d_6)**	**Acetone (d_6)**	**D_2O**	**DMSO (d_6)**	**Acetone (d_6)**	**D_2O**	**DMSO (d_6)**	**Acetone (d_6)**
33.19	4.03	4.08 4.11	4.42 4.48	3.12 3.57	3.07-3.11	3.4-3.69	5.64 - 6.05	5.51 6.19	5.73 - 6.37
16.59	4.02	4.06-4.10	4.40-4.47	3.12 3.57	3.06-3.1	3.4-3.71	5.63-6.04	5.51 6.19	5.69-6.75
3.13	4.02	4.05-4.09	4.37-4.44	3.12 3.57	3.05 3.1	3.4-3.7	5.65-6.04	5.51-6.19	5.7-6.35
0.38	4.02	4.04-4.076	4.37-4.41	3.12 3.57	3.04 3.08	3.4-3.7	5.6-6.00	5.53 6.19	5.7-6.35
0.06	4.02	4.01-4.05	4.32-4.39	3.12 3.57	3.04 3.08	3.4-3.7	5.62 6.0	5.53-6.20	5.7-6.35

Similar aggregation studies on oligomeric quaternary siloxane were carried out. The chemical shifts of $-N^+(C\mathbf{H}_3)_2$, $-N^+-C\underline{\mathbf{H}}_2-CH=CH_2$, $-CH=C\underline{\mathbf{H}}_2$ and $–C\underline{\mathbf{H}}=CH_2$ in the siloxane (E2) were monitored at concentrations ranging from 0.2 mM to 33 mM. There was no change in the chemical shift of the above-mentioned groups. This is a result of the association of oligomeric quaternary siloxane at the air -liquid interface instead of micellisation. Further studies would support the aggregation behavior of quaternary amino siloxanes.

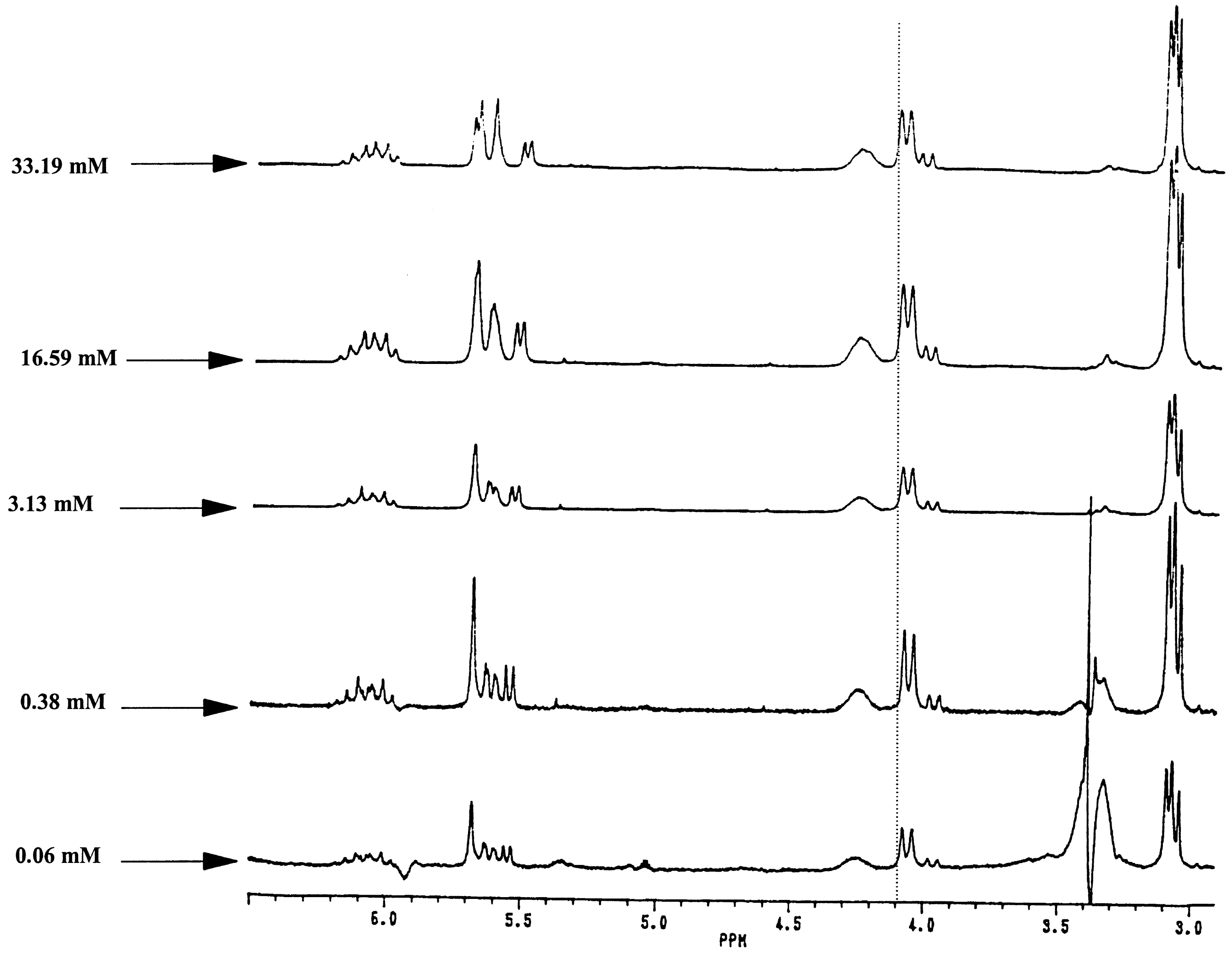


Figure 3. ^{1}H-NMR spectra of monomeric quaternary amino siloxane in DMSO-d_6 at various concentrations.

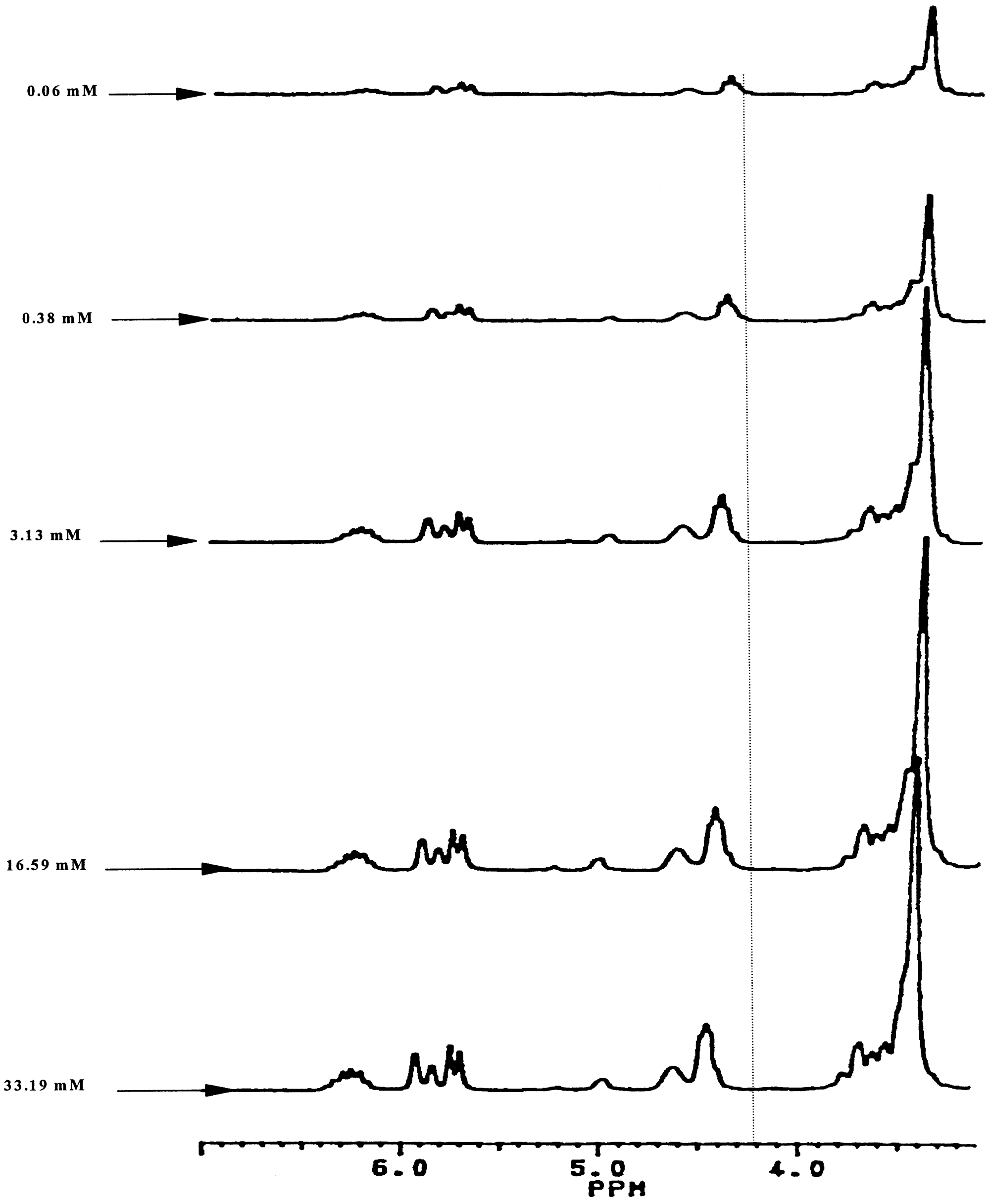


Figure 4. ^{1}H-NMR of monomeric quaternary amino siloxane in CD_3COCD_3 at variuos concentrations.

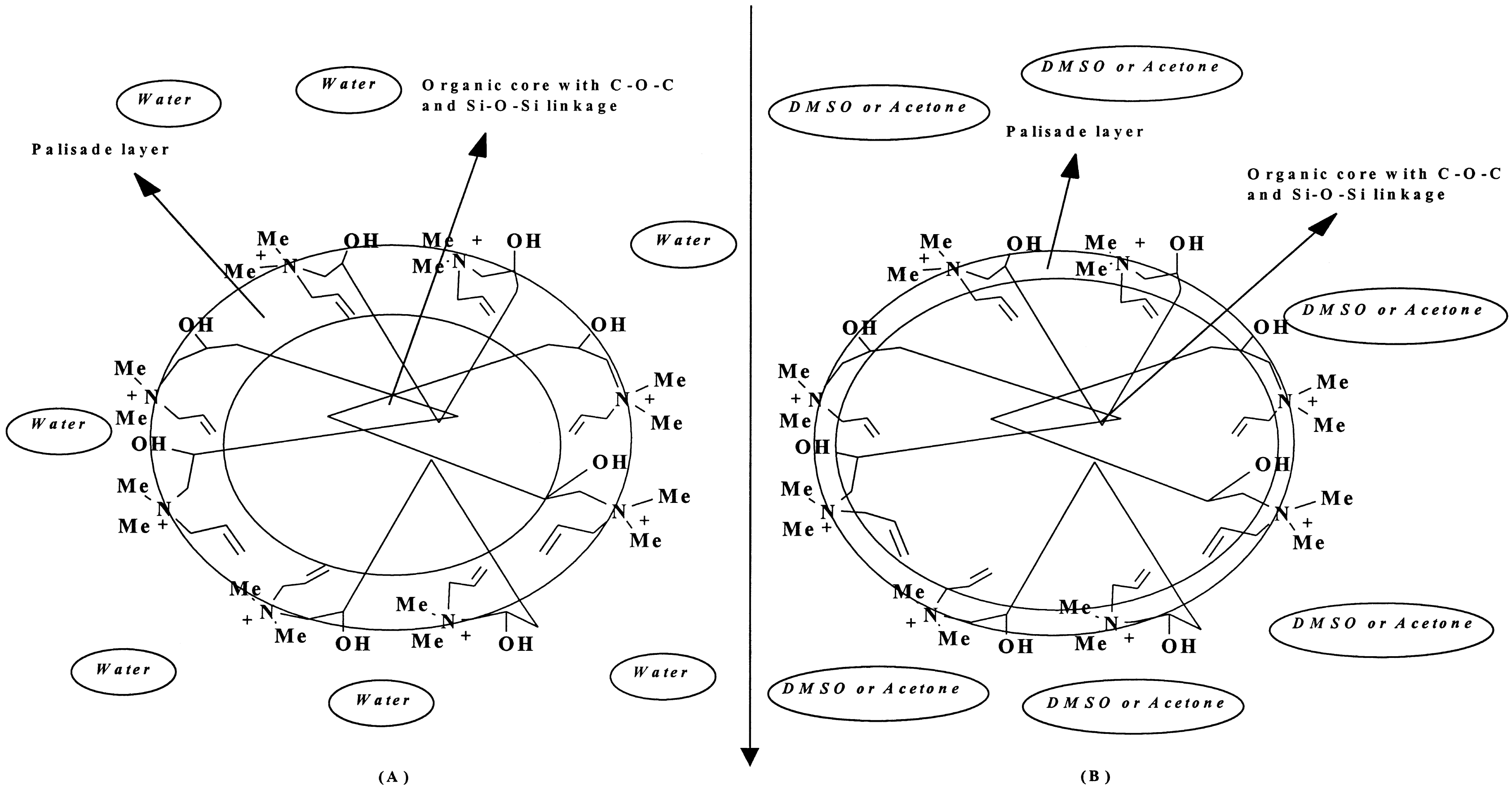


Figure 5. Schematic representation of aggregation behavior quaternary amino siloxane (D1) in (A) D_2O and (B) DMSO-d_6 or Acetone-d_6.

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CONCLUSION

Olefinic quaternary amino siloxane was prepared by reacting epoxy tetramethyl siloxane or oligomeric epoxy group containing siloxane with allylamine followed by quaternization. These quaternary amino siloxanes obtained showed excellent surfactant property. The lowering in surface tension was found to depend upon the number of siloxane units. Aggregation behavior of monomeric quaternary siloxane was studied by ^{1}H-NMR spectroscopy in polar solvents like D_2O, DMSO and CD_3COCD_3 by monitoring the change in chemical shift of groups attached to quaternary nitrogen. A shift in $-N^+-C\underline{\mathbf{H}}_2-CH=CH_2$ group chemical shift was observed in DMSO-d_6 and acetone-d_6 while there was no change in the chemical shift in water.

ACKNOWLEDGEMENTS

We are grateful to Hindustan Lever Research Foundation for financial support and also Dr. V. V. Kumar and Dr. R. G. Bhirud for their kind support during project work.

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Received November 20, 1997
Final revision received December 1, 1998

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