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The Solution Properties of Nonionic Oligosoaps Derived from Nonylphenol Formaldehyde Resin

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Nonionic oligosoaps (mol wt 6200 and 9700), consisting of a short polymer chain with chemically-attached soap-like groups, have been prepared from nonylphenol formaldehyde resin (mol wt 2000) by condensing 11 and 20 mol of ethylene oxide per nonylphenol ring making up the resin. Light-scattering, surface-tension, and vapor-pressure-depression measurements have been carried out. These oligosoaps formed agregates in water; the micellar weights were 81000 (11 mol condensate) and 70700 (20 mol), respectively, much as with the cationic oligosoap derived from polyallyl chloride reported elsewhere. The aggregation number, the dependence of the micellar weight on the sodium chloride concentration, the small surface area per molecule, in water, and the nonaggregation in nonaqueous solutions are discussed. It is noteworthy that these oligosoaps behave like monosoaps in various ways.

In a preceding paper,[1] we reported that a cationic polysoap (quaternization product (formura weight, 2770) of *N*-dodecyl-piperidine with polyallyl chloride (mol. wt, 650)), consisting of a short polymer chain with chemically-attached soap-like groups (designated as "*oligosoap*" below) formed a micelle in water. It seems that such an oligosoap generally forms a micelle in aqueous media. The occurence of this phenomenon in a nonionic oligosoap was ascertained in the present investigation.

Regarding an aqueous solution of ethylene-oxide condensates of alkylphenol formaldehyde resin, Yamashita[2] mentioned that the critical micelle concentration (CMC) of a dimeric resin derivatives was lower than that of the corresponding alkylphenol derivative (monosoap). Hayano *et al.*[3] reported that even those surfactants equal to the dimer did not show the CMC when treated by the method of determining the CMC for nonionic surfactants developed by Ross *et al.*

The present situation of the problem of the aggregation of these nonionic oligosoaps is similar to the early studies of the micelle formation of polyoxyethylated nonionic monosoaps. Namely, the physicochemical properties of the nonionic surfactant solutions changed gradually over a relatively wide surfactant concentration range depending upon the presence of a wide range of molecular sizes and impurities. Therefore, the CMC's of these surfactants were not definite and, further, differed from method to method among the CMC determination methods. On the other hand, numerous papers on the physicochemical properties of Pluronic polyol homologues in aqueous and nonaqueous media have appeared.[4,5] The present authors are especially interested in whether these polyols form a micelle or not.

Experimental

Determination of Molecular Weight Using a Vapor-pressure Osmometer (VPO). Determinations were carried out with a Mechrolab vapor-pressure osmometer, Model 302, at 37°C. The instrument was calibrated with solutions of benzil and methyl linolate over a concentration range of 0.004—0.05 mol solute/kg solvent. Steady readings of the resistance in ohms (ΔR) of these solutions were attained for more than 5 min in benzene and 15 min in *n*-butanol. The ΔR of the unknowns (oligosoaps) were divided by the weight concentration (C), and these quotients were plotted against C. The molecular weights were obtained by dividing the cali- bration constant by $(\Delta R/C)_{c\to 0}$.

Light Scattering (LS). Light-scattering measurements were carried out at a room temperature of about 21°C with a wavelength of 436 mμ, using a Shimadzu photoelectric light-scattering photometer. Scattered light was observed at 90°, 45°, and 135° relative to the incident beam. The optical clarification of the solution to be examined was made by centrifuge at 21000 g and filtration with an ultrafine sintered glass filter. Aqueous solutions were prepared by diluting an original solution volumetrically. After these solutions had been

1) Y. Ishigami and H. Narasaki, This Bulletin, **38**, 1852 (1965).
2) Y. Yamashita, *Yushi*, **14**, No. 11, 79 (1961).
3) W. Hayano, K. Kitagawa, T. Arai and K. Hattori, *Yukagaku (J. Japan Oil Chemists, Soc.)*, **13**, 33 (1964).
4) I. R. Schmolka and A. J. Raymond, *J. Am. Oil Chemists' Soc.*, **42**, 1088 (1965); C. W. Dwiggins, Jr., R. J. Bolen and H. N. Dunning, *J. Phys. Chem.*, **64**, 1175 (1960), *etc.*
5) J. M. G. Cowie and A. F. Sirianni, *J. Am. Oil Chemists' Soc.*, **43**, 572 (1966).

allowed to stand overnight, they were filtered by the filter directly into a light-scattering cell and measured. *n*-Butanol solutions were measured by successive dilutions of an original solution by filtering the solvent directly into the cell. The details have been given elsewhere.[1]

As a check on the entire calibration, the weight-average molecular weight ($\overline{M}_w$) of a standard polystyrene, Styron 683-7, supplied by the Asahi-Dow Co., was estimated by Hamashima and Hattori[6] by means of this instrument to be 234000; this value is in good agreement with the $\overline{M}_w$ values of 227000 for a column-fractionation method and 256000 for an ultracentrifuge.

Surface Tension. The surface-tension measurements were carried out by the drop-weight method in a thermostat maintained at 30.0±0.2°C, using the correction of Harkins and Brown.[7] More than two minutes were allowed for the formation of each drop of the solution in a saturated atmosphere (*cf.* Fig. 4).

Reagents. Nonylphenol was supplied by the Sanyo Yushi Kogyo Co.; the *p*- and *o*-nonylphenol contents were approximately 75% and 25%, respectively.[8] The benzene was dehydrated with sodium, and the *n*-butanol was dehydrated with calcium oxide. Methyl linolate supplied by Tanabe and Hashimoto,[9] was prepared from safflower oil; its minimum purity was found to be 98% (contained less than 2% methyl oleate) by gas chromatographic analysis. The other materials were reagent-grade materials.

Preparation of Oligosoaps. A mixture of 165 g (0.75 mol) of nonylphenol, 22.5 g (0.75 mol) of paraformaldehyde, and 225 m*l* of toluene were introduced, with 1.5 g of *p*-toluene sulfonic acid, into a two-necked 500 m*l*-flask, to which there were a reflux condenser and a thermometer. The reaction mixture was heated under reflux on an oil bath for 2.5 hr, and the resulting water was removed. The nonylphenol formaldehyde resin was then isolated by running the solution into stirred 90% methanol. The resin was purified by dissolving it in toluene and by adding this solution to 90% methanol; then it was dried at 60°C for 50 hr in a vacuum. The yield of the resin obtained was 44.5 g; its molecular weight was found to be $2.0\times10^3\pm100$ by means of VPO (the degree of number-average addition-condensation was 8.6).

Nonionic oligosoaps were prepared as follows, 15 g of the nonylphenol formaldehyde resin and 0.15 g of metallic sodium were dissolved in 45 g of xylene, after which ethylene oxide (EO) gas which had been dried through the layer of pellet pottasium hydroxide was bubbled into the solution at 120°C. The resulting products were poured into a 1 : 2 ether- *n*-hexane mixture. The precipitates were redissolved in methanol, and the solution was then treated with a great deal of *n*-hexane. An additional dissolution and precipitation were carried out. The oligosoaps were dried at 60°C for 50 hr in a vacuum. The EO contents of the compounds were determined by the weight increase in the EO condensation reaction. The oligosoap had the average EO chain lengths of 10.8 and 19.8 respectively per nonylphenol ring making up the nonylphenol formaldehyde resin molecule. These are abbreviated as NF-11 and NF-20 below. The corresponding molecular weights of these oligosoaps were $6.2\times$ and 9.7×10^3, respectively. A monosoap, NP-18, was similarly prepared from nonylphenol; it had an average EO chain length of 18.4 per mol.

Results and Discussion

Light Scattering of Aqueous Solutions. The reduced-intensity *vs.* oligosoap-concentration curves are shown in Fig. 1. The CMC's of the aqueous oligosoap solutions (NF-11: $6\times$; NF-20: 5×10^{-6} mol/*l*) corresponding to the sharp breaks on these curves are in good agreement with the inflection points (CMC: both, 2×10^{-6} mol/*l*) observed in the surface-tension *vs.* log-concentration curves, as is shown in Fig. 3. These CMC values (the order of 10^{-6} mol/*l*) of the oligosoaps are much smaller than that found for the monosoap (the order of 10^{-4} mol/*l*). The Debye plots of the oligosoaps in aqueous solutions are illustrated in Fig. 2. These CMC's and the micellar weights of these oligosoaps are given in Table 1. The micellar weights and the aggreagation numbers in water were 81000 and 13.0 in NF-11, and 70700 and 7.3 in NF-20.

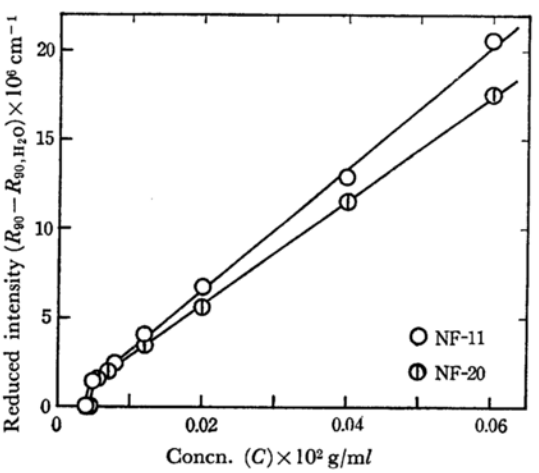

Fig. 1. Reduced intensity *vs.* concentration curves in water. (Wavelength 436 mμ, 21°C)

It was found that these nonionic oligosoaps formed aggregates in aqueous solution, much like the cationic oligosoap derived from polyallyl chloride already reported.[1] The micellar weights and the aggregation numbers of the cationic oligosoap were 18800 and 7.0 in water, 32300 and 11.8 in a 0.3 M aqueous sodium chloride solution. Taking account of the contribution of the presence of the

6) M. Hamashima and S. Hattori, *Tokyo Kogyo Shikenjo Hokoku (Reports of The Government Chemical Industrial Research Institute, Tokyo)*, **62**, 247 (1967).
7) W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, **41**, 499 (1919).
8) H. Narasaki, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 391 (1963).
9) K. Tanabe and T. Hashimoto, *Yukagaku (J. Japan Oil Chemists' Soc.)*, **16**, 611 (1967).

Table 1. The micellar properties of the nonionic oligosoaps in water and aqueous sodium chloride solutions as determined by light scattering

	NaCl mol/l	CMC mol/l $\times 10^6$	$\overline{M}_w$[b] $\times 10^{-3}$	n[c]	A_2[d] mol·cm^3/g$^2 \times 10^4$	dn/dc[e] ml/g
NF-11	0	6	81.0	13.0	0.4	0.172
	0.1	5	77.1	12.4	−0.2	0.169
	0.5	3	82.3	13.3	−0.5	0.169
	1.0	2	95.1	15.3	−4.9	0.169
	2.0[a]	<2	177.9	28.6	−3.7	0.169
NF-20	0	5	70.7	7.3	1.6	0.158
	0.1	4	68.2	7.0	1.8	0.158
	0.5	2	63.1	6.5	1.2	0.158
	1.0	1	58.8	6.0	0.9	0.158
NP-18	0	200	52.0	51	1.6	0.146

a) Dissymmetry is 1.04. The others are 1.00.
b) Weight-average micellar weight.
c) Aggregation number. The molecular weights of NF-11 and NF-20 employed in the calculation were 6210 and 9720, respectively.
d) Second virial coefficient.
e) Refractive index increment, $\Delta n/\Delta(C-\mathrm{CMC})$.

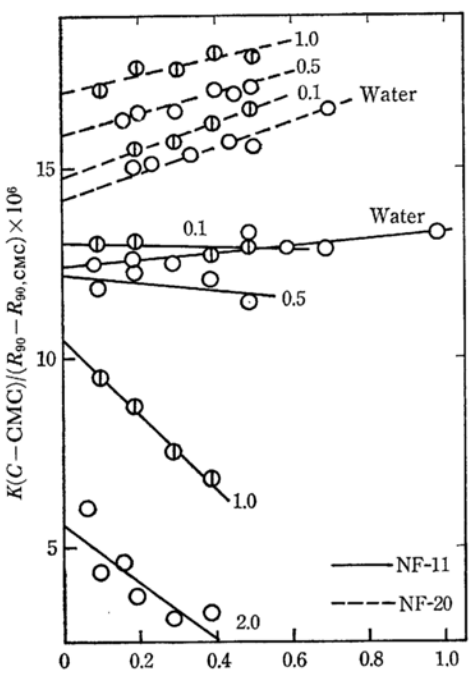

Fig. 2. Light scattering of the oligosoaps in water and aqueous sodium chloride solution (wavelength 436 mμ, 21°C). Numericals in this figure show the concentration of sodium chloride (mol/l).

molecular-weight distribution for $\overline{M}_w$, or account of the possibility of the presence of a small number of very large particles to be mentioned below, the aggregation numbers of these oligosoaps may be smaller than the results shown in Table 1. In this manner, we concluded that these oligosoaps formed aggregates even in quite lower oligosoap concentration ranges, and that the aggregation numbers of these oligosoaps were relatively small.

The Effect of Added Sodium Chloride on Light-scattering Results. The effect of added sodium chloride on the CMC's and the micellar weights of the oligosoaps are included in Fig. 2. and Table 1. The micellar weight of NF-11 increased with an increase in the salt concentration except for the case of the 0.1 M salt concentration; namely, the aggregate grew from 81000 in water to 177900 (dissymmetry 1.04) in 2 M salt concentration. At the same time, the second virial coefficient (A_2) decreased gradually with an increase in the salt concentration.

This behavior was reversed for NF-20. A decrease in the micellar weight was observed with an increase in the salt concentration. The A_2 was little affected by the salt.

On the other hand, the CMC's of both NF-11 and NF-20 declined upon the addition of salt, although the CMC values are too low to estimate accurately. Such a behavior of NF-20 was different from the well-known fact that the addition of salt causes a decrease in the CMC and an increase in the micellar weight in ordinary ionic monosoaps.

Related results have been reported for polyoxyethylene alkyl ether by Becher,[10] and Schick *et al.*[11] Becher theorized that the added salts had no appreciable shielding effect on the micellar charge of higher EO condensates, whereas a

10) P. Becher, *J. Colloid Sci.*, **17**, 325 (1962).
11) M. J. Schick, S. M. Atlas and F. R. Eirich, *J. Phys. Chem.*, **66**, 1326 (1962).

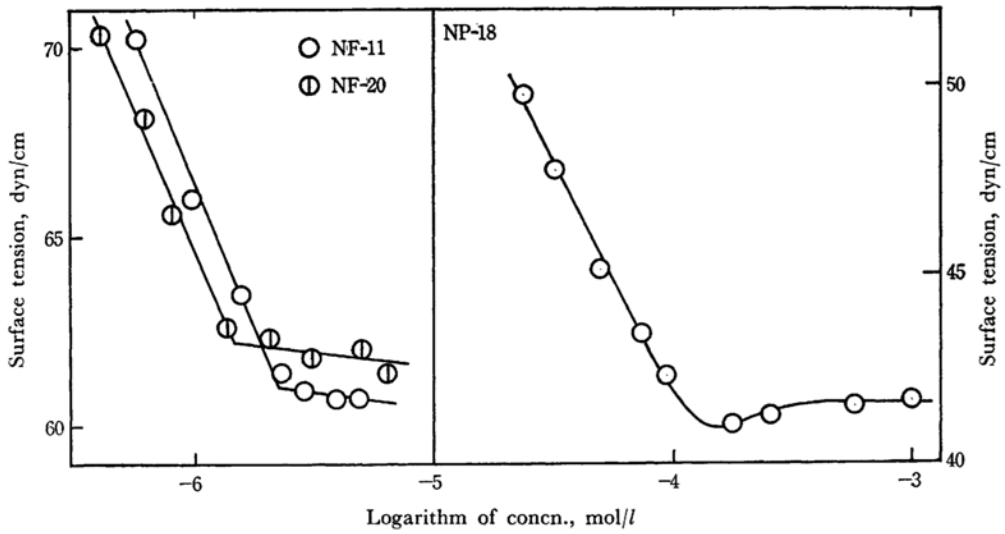

Fig. 3. Surface tension *vs.* logarithm of concentration curves at 30°C by the drop-weight method.

significantly larger charge on a single molecule (produced by the formation of hydronium ion) was smeared out into the interior of a micelle if the extension of the EO chains was at all great. Consequently, the effect of the added salt would be to lower the double-layer potential of the individual monomer molecules and render their incorporation into the micelle easier. In another way, this would seem to indicate that the dehydration effect of the added salt was minor for the higher EO condensates. For the lower EO condensates, he considered the result to be incipient coacervation rather than the formation of large micelles upon the addition of salt. Thus, he explained why the micellar weight of higher EO condensates remained unchanged upon the addition of salt in his cases. However, he did not explain why it decreased in other cases.

Schick *et al.* postualted that the increased length and lower solubility of EO chain enhanced the absorption of Na^+ to such an extent that it increased the overall solubility of the nonionic surfactant. In this case, they did not take the decrease in the CMC value into consideration.

Further, Becher pointed out that the EO contents in each EO condensate homologue in which the apparent size of the micelle did not increase upon the addition of salt, were about 70—75% of the EO by weight per molecule. The EO contents of NF-11 and NF-20 were 68 and 79% respectively. Therefore, the solution behavior of the oligosoaps under consideration here was consistent with Becher's results. It is noteworthy that these phenomena can be seen in the oligosoaps as well as in monosoaps.

From the viewpoint of the steric configuration of the oligosoaps, adjacent *p*-nonylphenol rings connected with a methylene group can not exist on the same plane because of the steric hindrance between the O atom of the 1-position and the *m*-H, or between the *m*-H of the nonylphenol ring themselves. This is true in the case of *o*-nonylphenol. Therefore, the aggregates of these oligosoaps perhaps form a crowded and interpenetrated structure in aqueous solutions. Namely, the aggregates may easily form intramolecular and intermolecular interpenetrated structures between the lyophilic and the EO groups making up these oligosoaps. Therefore, Becher's smearing-out effect of the charges into the aqueous portion of the micelle can take place, in NF-11 as well as in NF-20, because such interpenetrated structures can form in both NF-11 and NF-20 independent of the EO chain lengths of these oligosoaps. However, the results observed did not support this. Presumably we can interpret this phenomenon by the possibilities that there are two patterns in the hydration of the EO chain, for lower and higher EO condensates, or that the effect of the added salt concentration on the micellar weight of any EO condensate homologues can be divided into two regions which are combined at such a minimum micellar weight as for 0.1 M salt in the case of NF-11. The A_2 of NF-11 became negative and that of NF-20 remained positive upon the addition of salt, as is tabulated in Table 1. This appears to support this assumption that the hydrations of these micellar surface layers are different from one another.

Moreover, it would seem to be possible for us to consider separately the effect of added salt on a single molecule and on a micelle in explaining this phenomenon.

Surface-tension Results. The relations of the surface tension (γ) *vs.* the logarithm of concentration (C) are given in Fig. 3. The apparent

surface tension *vs.* the time required for each drop formation curves as determined by the drop-weight method are shown in Fig. 4. There are evident inflection points at about 2×10^{-6} mol/*l*, corresponding probably to the CMC and then a gentle descent of the γ follows.

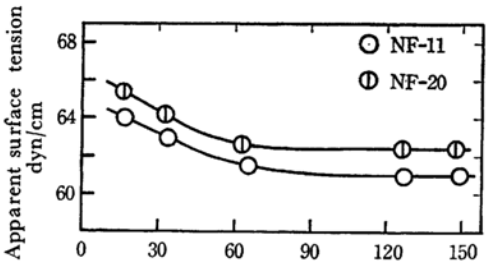

Fig. 4. Apparent surface tension *vs.* the time required for each drop formation curves at 30°C by the drop-weight method NF-11 : 2.90×10^{-6} mol/*l*; NF-20: 2.06×10^{-6} mol/*l*.

In view of the presence of the molecular-weight distribution in the oligosoaps under consideration here, the selected adsorption of smaller members of the molecules at the air-solution interface is, of course, to be expected. However, these oligosoaps show evident inflection points in the γ-log C plots and make straight lines below the concentration of the inflection points in the aqueous solutions. Therefore, in order to compare them approximately with monosoaps, we estimated the surface excess (Γ) and the corresponding surface area per molecule (A) of the oligosoaps at the air-solution interface from the slopes below the concentration of the inflection points by applying Gibbs adsorption isotherm, $\Gamma=-d\gamma/(\boldsymbol{R}T\,d\ln C)$, and $A=10^{16}/\boldsymbol{N}\Gamma$, where $\boldsymbol{R}$ is the gas constant; T is the absolute temperature; and $\boldsymbol{N}$ is the Avogadro number. The results obtained are listed in Table 2; they are of the same order of magnitude as that of monosoap, which is consistent with the findings concerning the cationic oligosoap reported on previously.[1] Moreover, the A values of NF-11 and NF-20 are almost the same. The small A values can be explained if the smaller molecules included in the oligosoaps are selectedly adsorbed at the air-solution interface at higher densities as a result of the Van der Waals attractive force.

Table 2. Surface tension results in water

	CMC mol/*l* $\times10^6$	Γ[a] mol/cm^2 $\times10^{10}$	A[b] Å^2/mol
NF-11	2	3.00	55
NF-20	2	2.58	64
NP-18	150	2.21	75

a) Surface excess calculated from the slopes of γ-log C plots below the CMC.
b) Corresponding surface area per molecule.

The Properties of Nonaqueous Solutions. The molecular weights of the nonionic oligosoaps under consideration here were determined in benzene and *n*-butanol by means of vapor-pressure depression (VPO) and light-scattering (LS) measurements. The results obtained are summarized in Table 3. The number-average molecular weight

Table 3. The molecular weights in nonaqueous solutions as determined by vapor pressure depression and light scattering

	$M(w, inc)$[a] $\times10^{-3}$	VPO $\bar{M}_n\times10^{-3}$		LS[c] $\bar{M}_w\times10^{-3}$
		benzene	*n*-butanol	*n*-butanol[d]
NF-11	6.2_1	7.0±0.5	5.4±0.5	18.6
NF-20	9.7_2	9.5±0.7	—[b]	25.9

a) Molecular weight determined by the weight increase in the ethylene oxide condensation reaction.
b) Turbid in the concentration range capable of determination.
c) Light scattering measurements in benzene were not made because dn/dc values were small and scattered.
d) NF-11: $A_2=1.6\times10^{-4}$, $dn/dc=0.106$
NF-20: $A_2=1.6\times10^{-4}$, $dn/dc=0.096$

($\bar{M}_n$) of NF-11 was 7000 (9500 in NF-20) in benzene and 5400 in *n*-butanol, as determined by means of VPO. These values were in tolerable agreement with the molecular weights ($M(w, inc)$) of 6200 in NF-11 and 9700 in NF-20 as determined from the weight increase in the EO condensation reaction. Therefore, it can be said that these oligosoaps did not form an aggregate in these solvents. The weight-average molecular weights ($\bar{M}_w$) of NF-11 and NF-20 were 18600 and 25900 in *n*-butanol, respectively, as determined by means of LS. Although the light-scattering results in *n*-butanol would suggest the formation of an aggregate, it would be possible to suppose that the oligosoaps did not aggregate; this seems possible because of approximate agreement with $\bar{M}_n$ and $M(w, inc)$, and because of the presence of molecular-weight distribution. It may be suggested that the difference between $\bar{M}_n$ and $\bar{M}_w$ is partly caused by a polydispersity in the micellar weight. Some reports have appeared to support this assumption.

Corkill, Goodman, and Walker[12] have shown that the $\bar{M}_w$ of Aerosol OT by LS diminishes in toluene with the time of aging after the preparation of the solution, at last reaching the same level as the $\bar{M}_n$ obtained by VPO, which remained constant independent of the solution's age. This phenomenon was attributed to a very small number

12) J. M. Corkill, J. F. Goodman and T. Walker, *Trans. Faraday Soc.*, **61**, 589 (1965).

of very large aggreagtes, which were formed by small quantities of water (or impurities) in the fresh solutions.

Cowie and Sirianni[5] showed that the $\overline{M}_w$'s of Pluronic polyol homologues were larger for the values determined from LS than for those determined from ultracentrifuge in water, butyl chloride, and dioxane. They explained this phenomenon by postulating the presence of a small number of large clusters which could be observed by LS but which were disrupted under the influence of the strong force field experienced in the ultracentrifuge, or by postulating the presence of a very broad spectrum of molecular sizes in the system. Therefore, nonaggregation of these oligosoaps is conceivable.

As has been mentioned above, it is noteworthy that such an oligosoap behaves like a monosoap in various ways. This indicates that such an oligosoap molecule is not as immobile as might be expected from its crowded and interpenetrated molecular structure.

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