

Comparing didecylmethylamine oxide with stearyldimethylamine oxide

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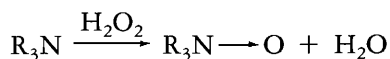
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Synopsis

Didecylmethylamine oxide is potentially useful as a hair conditioner in both shampoos and rinses. It can be prepared as an 80% active aqueous fluid which offers several advantages, including formulation versatility and ease of handling. The physical properties and general conditioning activity of didecylmethylamine oxide differ significantly from those of stearyldimethylamine oxide, a structural analog.

INTRODUCTION

Alkyldimethylamine oxides are well-known compounds having a variety of commercial applications. When the alkyl substituent is in the coco range, these amine oxides serve as foam boosters in shampoos (1) and in light duty liquid detergents (2). Representative of the larger alkyl groups, stearyldimethylamine oxide (SDMAO) is an effective hair conditioner (3). This type of amine oxide is readily prepared through oxidation of the corresponding tertiary amine with hydrogen peroxide (4,5).



Surprisingly, dialkylmethylamine oxides are virtually unreported in the chemical literature. Didecylmethylamine oxide (DDMAO) is an example of this type of compound. This amine oxide can be prepared as an aqueous system at concentrations up to 80% active (6). This concentration gives obvious handling advantages over the more dilute alkyldimethylamine oxides reported in the literature.

Didecylmethylamine oxide and stearyldimethylamine oxide possess similar empirical formulae but very different molecular geometries (Figures 1 and 2). The differing molecular geometries result in significantly altered physical properties and interactions with hair.

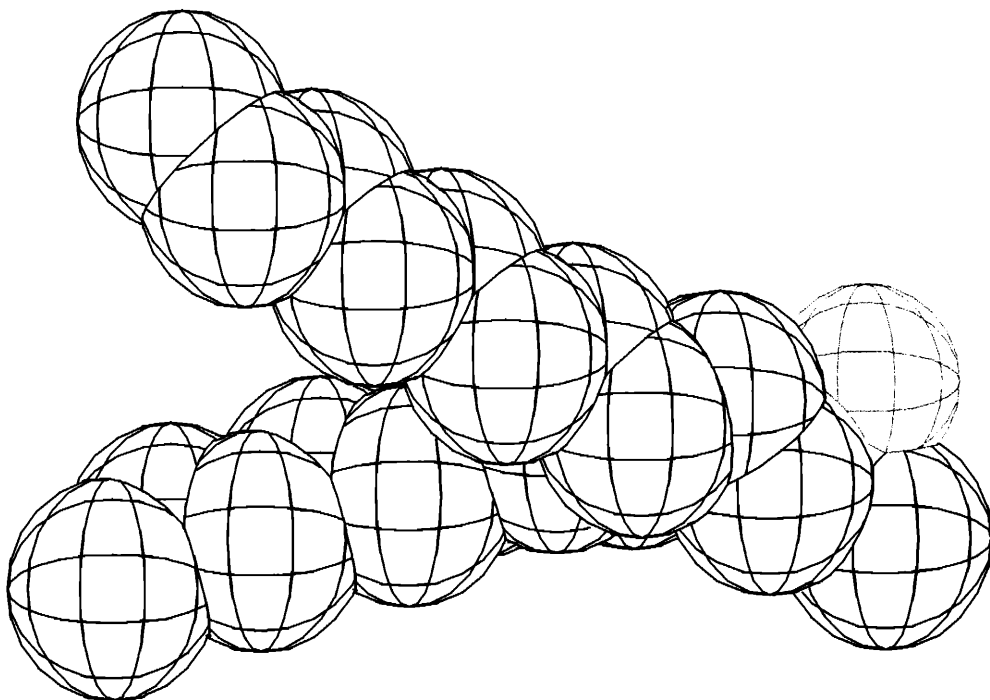


Figure 1. SPACEFILL representation of didecylmethylamine oxide.

EXPERIMENTAL

INSTRUMENTATION

Spectral data were obtained using the amine oxides as supplied. Nuclear Magnetic Resonance spectra, proton and carbon-13, were run on a GE/Nicolet NT-360 instrument. Viscosity measurements were made using a Haake Rotovisco-RV viscometer.

MODELING OF MOLECULAR GEOMETRY

Molecular Design Ltd's (San Leandro, CA) PRXBLD and SPACEFILL programs were used to depict local low-energy conformations for single molecules of SDMAO and DDMAO.

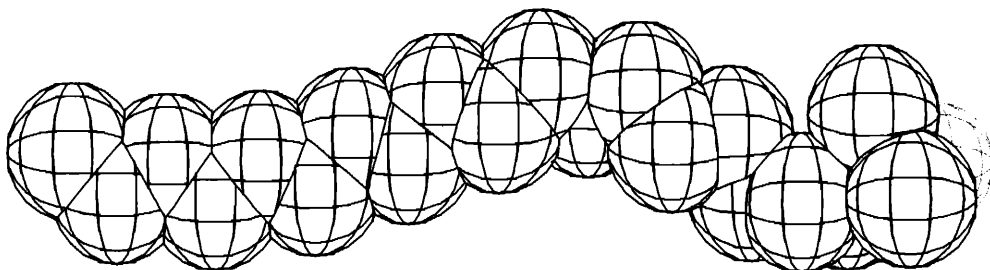


Figure 2. SPACEFILL representation of stearyl dimethylamine oxide.

TOXICOLOGICAL SUMMARY

The oral LD₅₀ of DDMAO in rats (combined sexes) is 894 mg/kg. The dermal LD₅₀ on rabbits is greater than 2000 mg/kg. No genotoxic activity is demonstrated by this chemical in the *Salmonella*/microsome assay and the Rat Hepatocyte Primary Culture/DNA Repair Test: Test performed by Hilltop Laboratories, Cincinnati, Ohio.

Concentrated DDMAO (80 weight percent in water) is an eye irritant in rabbits and causes delayed burns to the skin. When tested on rabbits in dilute form (1 wt % active in water), this amine oxide was not an eye irritant. However, skin irritation was noted after 4 hours of exposure. This irritation was reversible.

PREPARATION OF FORMULATIONS

Skeleton shampoo and conditioner solutions were prepared in a similar manner: The conditioning agent was dissolved in deionized water preheated to 40°C. With the temperature constant, the remaining components were sequentially added with vigorous stirring. The pH of each solution was about 6.9 and was not adjusted.

SOIL TOLERANCE OF SHAMPOOS

To compare the effects of DDMAO and SDMAO on foam production, prototype shampoos prepared with each of these amine oxides were evaluated in the presence of an artificial soil (olive oil). Formulations were prepared, diluted to working concentrations (0.01, 0.025, 0.05, 0.10 weight percent), and heated to 49°C. A 100-ml aliquot of the diluted shampoo was transferred to a 500-ml stoppered graduated cylinder and rotated ten times by hand through 180 degrees. The foam generation test was replicated in triplicate in both the absence of artificial soil and the presence of 2g of olive oil.

FOAM EVALUATION

The foam-generating characteristics of both shampoo and conditioning formulations were measured using the Ross-Miles procedure (ASTM D1173-53). Water hardness levels of 50 and 150 ppm (as CaCO₃) were used.

HAIR CONDITIONING PROPERTY COMPARISON

The formulations represented by shampoos A–D and rinses E–N were diluted with deionized water to 5 wt %, and then heated to 40°C. For each formulation, a 4-g brown hair tress from 10-in European hair (DeMeo, New York) was dipped fifty times in the diluted system, patted between towels to remove excess liquid, dipped fifty times in clean deionized water as a rinse, and again patted semi-dry. The tress was then combed out with a fine-tooth hard-rubber comb. The number of comb strokes to remove all tangles and the drag on the comb were noted. This entire procedure was replicated in triplicate, providing a variation in wet-comb untangling of ± 2 comb strokes. The degree of drag was a subjective determination.

Finally, the hair tress was air-dried at 25°C and 70% relative humidity for 24 hours. Immediately after combing the tress, its flyaway was recorded as the distance from the median of the tress to its outermost point on a horizontal line. Variation between the

three replicates for this evaluation averaged ± 0.8 cm. Between each measurement, static charge on the comb was discharged using a Staticmaster discharge pistol. The entire evaluation was conducted as a blind test by three persons.

RESULTS AND DISCUSSION

PHYSICAL PROPERTIES

Several physical properties were determined and are compared for DDMAO and SDMAO. A summary of these values is given in Table I.

Although didecylmethylamine oxide and stearyl dimethylamine oxide are closely related, their physical properties were found to be significantly different. In view of the interrelationship of many physical properties, solubility, and micelle formation, it is not surprising that such a broad range of characteristics differed for the two compounds (7).

From a formulator's standpoint, DDMAO should be easier to handle than SDMAO, on the basis of more favorable pour point, gel point, and lower viscosity. The data summarized in Tables I and II support this conclusion, in that DDMAO could be obtained in liquid form at much higher concentrations than could SDMAO. Figure 5, depicting the gel/liquid profiles as a function of temperature and concentration, also supports more facile handling properties for DDMAO.

While it was possible to observe a cloud point for the DDMAO at concentrations of 40% or less, SDMAO consistently gelled and prevented our obtaining its corresponding value at all concentrations tested.

Table I
Summary of Amine Oxide Physical Property Comparisons

	DDMAO	SDMAO
Formula	$C_{21}H_{45}NO$	$C_{20}H_{43}NO$
Molecular weight	327	313
Content, as received		
Active (wt %)	82.3	23.4
H ₂ O (wt %)	17.7	76.6
Physical Constants ^a		
Density at 65°C (g/cc)	0.8675	0.947
Viscosity, 60°C (cp)	54	N.A.
60°C, 10% aq. mixture (cp)	<1	248
Pour point (°C)	21	50
Gel point (°C)	15	59
10% aq. mixture (°C)	<0	44
Cloud point, 10% aq. fluid (°C)	10	gelled
HLB value ^b		
Calculated	7.8–8.3	8.3–8.8
Experimental value	6, 8	5.5–6
pKa (Isopropyl alcohol)	3.3	3.6

^a Amine oxides were used as received, unless otherwise noted.

^b See reference 8 for experimental procedure.

Table II
Viscosity Profiles of Amine Oxides

$\begin{array}{c} \text{CH}_3 \\ \\ \text{Viscosity* of } \text{C}_{18}\text{H}_{37}\text{N} \rightarrow \text{O} \text{ vs Temperature/Concentration} \\ \\ \text{CH}_3 \end{array}$		
	Conc. (wt %)	
Temp (°C)	10	20
60	248	242 (@61°C; sample off-scale @ 60°C)
65	141	156
70	85	131

Temperature range below 60°C resulted in very high viscosities for SDMAO.

$\begin{array}{c} \text{CH}_3 \\ \\ \text{Viscosity* of } \text{C}_{10}\text{H}_{21}-\text{N}-\text{C}_{10}\text{H}_{21} \text{ vs Temperature/Concentration} \\ \\ \text{O} \end{array}$				
	Conc. (wt %)			
Temp (°C)	10	20	70	82
30	—	—	87	229
40	8.3	38	51	117
50	2.6	4.5	37	70
50	<1.0	3.0	31	54

* In CENTIPOISE, as measured via HAAKE ROTOVISCO-RV viscometer.

Several attempts to measure effective hydrophile-lipophile balance (HLB) values for the amine oxides with conventional techniques met with considerable difficulty (8,9). By either of the two procedures used, though, comparable results were obtained for both compounds.

Table III shows solubility to be a major difference in the physical properties of DDMAO and SDMAO. At room temperature and a 1% by-weight active level, SDMAO was readily soluble in water, whereas DDMAO was insoluble. In view of DDMAO's insolubility in water, it may seem inconsistent that at 82% DDMAO in

Table III
Summary of Solubilities* of Amine Oxide

Solvent	DDMAO ($\text{C}_{10}\text{H}_{21}$) ₂ CH ₃ NO	SDMAO $\text{C}_{18}\text{H}_{37}(\text{CH}_3)_2\text{NO}$
Water	Insoluble	Soluble
Mineral oil	Soluble	Insoluble
Ethanol	Soluble	Soluble
Acetone	Soluble	Soluble

* Measured as a 1 wt % active solution (23°C, neutral pH) in solvent.

water, a clear homogeneous fluid was obtained. However, inspection of Table IV reveals the cloud point of the dilute DDMAO liquid to be below ambient temperature (10°C) while the cloud point of the concentrated liquid is above room temperature (>65°C). Microscopic inspection of the concentrated DDMAO system did not show evidence of a microemulsion or a liquid crystalline phase, suggesting that DDMAO is the continuous phase for the concentrated solution.

Values for the pKa's of DDMAO and SDMAO are also reported in Table I. These determinations were conducted in isopropanol to compare values which were obtained under identical conditions: a 1% by-weight solution of amine oxide in isopropanol at 23°C. The results suggest that both amine oxides have a similar basicity. However, during this study, it was noted that protonated DDMAO forms a white precipitate in both isopropanol and water while no precipitate occurs with SDMAO.

MOLECULAR GEOMETRY

Figures 1 and 2 are SPACEFILL representations of a low-energy conformation of an isolated molecule of each of the amine oxides. Figures 3 and 4 are the corresponding ORTEP representations of the amine oxides. These figures suggest that a greater steric hindrance about the N-O moiety of the dialkyl amine derivative could suppress access of polar molecules to that functionality, resulting in significantly different physical properties from those of the structural analog SDMAO.

The hindered access of polar molecules (water, for example) to the hydrophilic portion of DDMAO is believed to at least partially explain the unusual phase behavior and solubility of this amine oxide in water. However, water should have ready access to the hydrophilic portion of SDMAO, resulting in a greater degree of water solubility for SDMAO than for the twin-tailed amine oxide.

The wide fluid range of DDMAO can also be ascribed to the compound's molecular

Table IV
Cloud Points of Amine Oxides

Conc. (wt %)	Cloud points (°C)	
	DDMAO (C ₁₀ H ₂₁) ₂ CH ₃ NO	SDMAO C ₁₈ H ₃₇ (CH ₃) ₂ NO
1.0	10	<0
10.0	10	b
15.0	10	b
20.0	10	b
23.4	—	a,b
30.0	12	—
40.0	23	—
50.0	b	—
55.0	b	—
60.0	b	—
70.0	>65	—
82.3	>65 ^a	—

^a Undiluted material.

^b Gel prevented measurement.

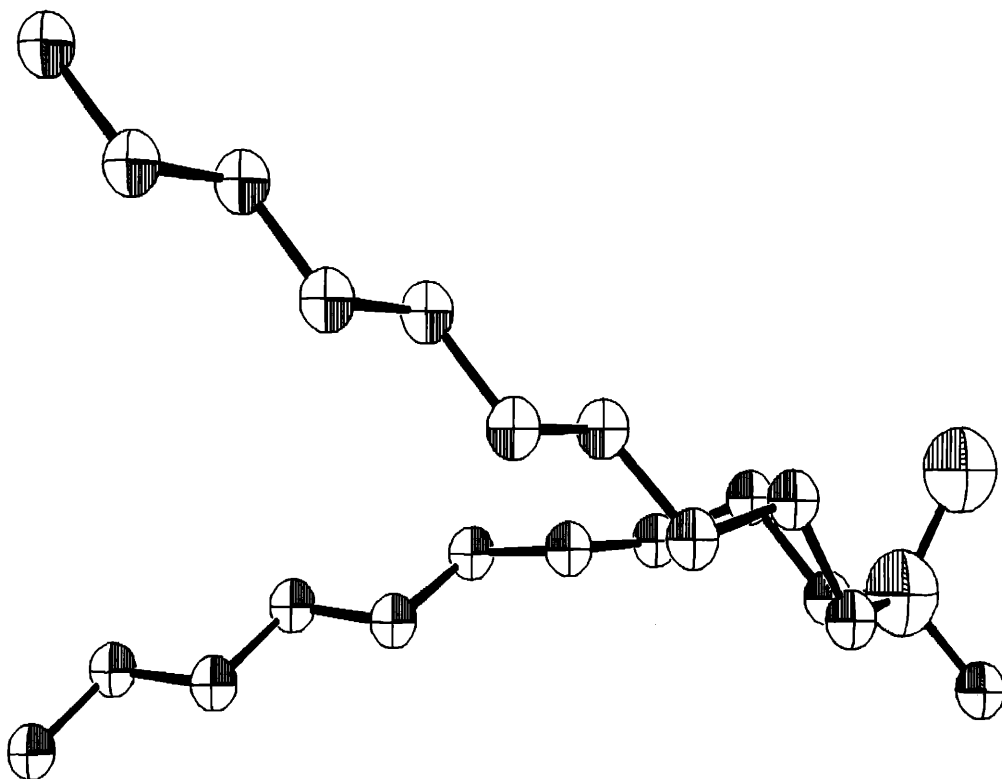


Figure 3. ORTEP representation of didecylmethylamine oxide.

geometry. The two fatty alkyl substituents of DDMAO should hinder a close packing of amine oxide molecules, resulting in a greater tendency to resist gellation than experienced for the single-tailed SDMAO.

The pK_a 's of the two amine oxides were found to be very similar. While this observation appears to be inconsistent with the differences in other properties, it can be explained when the very small size of a proton is considered. In spite of the differences in the steric hindrance of the DDMAO and SDMAO, the proton may be so small that little, if any, actual hindrance is encountered in the protonation of the oxygen.

SHAMPOO FORMULATIONS

Since the physical properties of DDMAO and SDMAO were significantly different, it was hypothesized that the two compounds would behave differently in the presence of

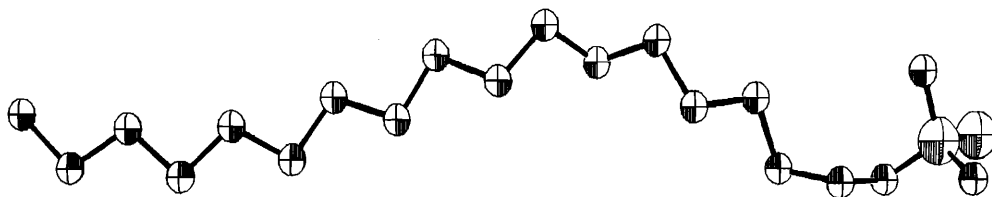


Figure 4. ORTEP representation of stearyltrimethylamine oxide.

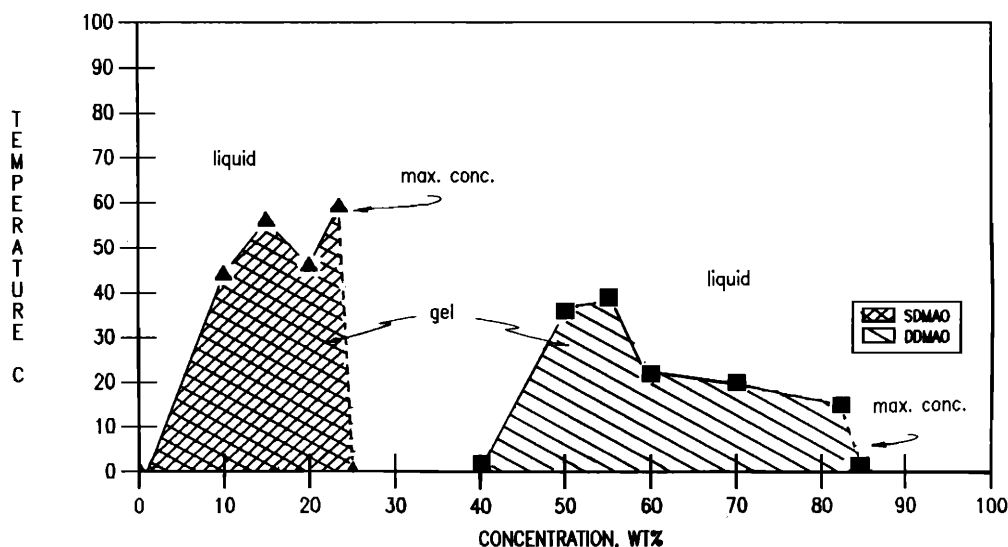


Figure 5. Aqueous systems of DDMAO and SDMAO.

an anionic surfactant. In view of the growing popularity of conditioning shampoos, which might be expected to contain both an amide oxide and an anionic surfactant, the two amine oxides were compared in a neutral conditioning shampoo formulation. The compositions of the shampoo formulations are given in Table V.

In experiments comparing the conditioning properties of these formulations, the two amine oxides gave comparable control of flyaway when used at 2% by-weight in a shampoo (see Table VI). DDMAO, however, produced a slightly sticky feel to hair at this concentration. This is partially ascribed to the unusual solubility of this compound. A lower concentration (0.5 wt %) of DDMAO resulted in a loss of flyaway control, although tangling characteristics of the hair tress were improved (e.g., formulations containing 0.5 wt % DDMAO gave untangling activity comparable to 2.0 wt % SDMAO). Due to the total insolubility of DDMAO under acidic conditions, the role of pH was not examined.

The effects of each amine oxide on foam characteristics of the shampoo were compared. Figures 6–9 reflect the foam profile of shampoos B–D using the Ross-Miles procedure

Table V
Shampoo Formulations* Containing Amine Oxides

Component	Weight % (active basis)			
	A	B	C	D
Ammonium lauryl sulfate	15	15	15	15
Lauryldiethanolamide	3	3	3	3
Stearyldimethylamine oxide	0	0	0	2
Didecylmethylamine oxide	0	0.5	2	0
Water (deionized)	82	81.5	80	80

* pH = 6.9 (unadjusted).

Table VI
Combing Behavior of Hair Treated With Shampoo Containing Amine Oxides

Formulation	Wet comb		Dry comb		
	Strokes to Untangle	Drag	Flyaway (cm)	Appearance	Feel
A	20 +	Moderate	4.6	Frizzy	Coarse
B	8	Slight	4.0	Nearly straight	Soft
C	20	Moderate	2.3	Curl retained	Sticky
D	10	Moderate	2.5	Curl retained	Soft

(10) as a simple means of comparison rather than actual shampoo performance evaluation. In general, all the foams generated in this study were of a small cell variety. Shampoo D, containing 2% SDMAO, foamed more than did shampoo formulation C, containing 2% DDMAO. At a level of 0.5% DDMAO in shampoo B, foaming characteristics of formulations B and D were similar, though. Interaction of the anionic component with calcium ions did not alter the relative effects of the two amine oxides. Thus, DDMAO might be expected to suppress foam to a greater extent than SDMAO in a conditioning shampoo formulation.

Table VII compares the foam stability of shampoos containing each amine oxide in the presence of artificial soil (olive oil). Formulations containing 2% of either amine oxide (formulations C and D) retained only 40% of their initial foam at a shampoo concentration of 0.10% or less. Formulation B (0.5% DDMAO) retained 95% of its initial foam at 0.10% usage.

In summary, the differences in the physical properties of DDMAO and SDMAO are reflected in the activity of these compounds in a general shampoo formulation. A shampoo containing DDMAO had untangling and soil tolerance activity which were judged superior to a shampoo containing SDMAO near neutral pH. However, the lack

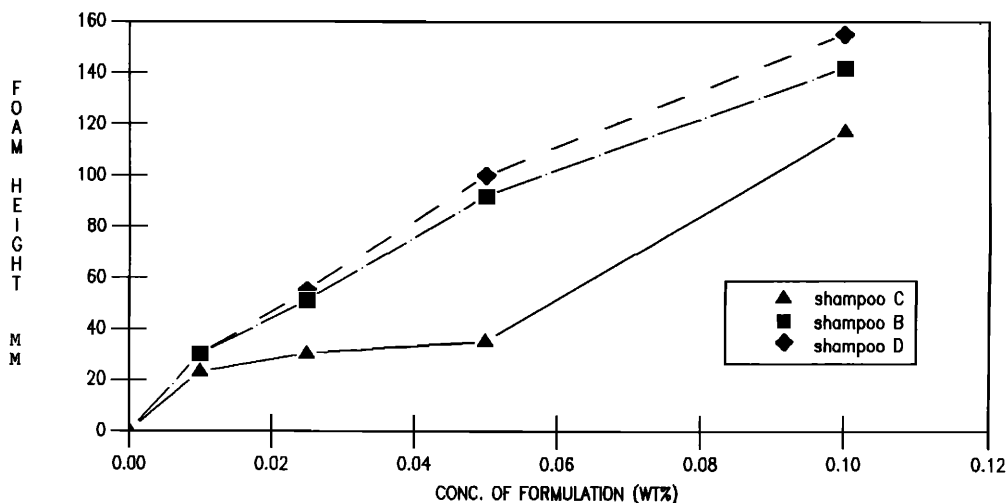


Figure 6. Foam height ($T = 0$ min). 50 ppm CaCO_3 in water.

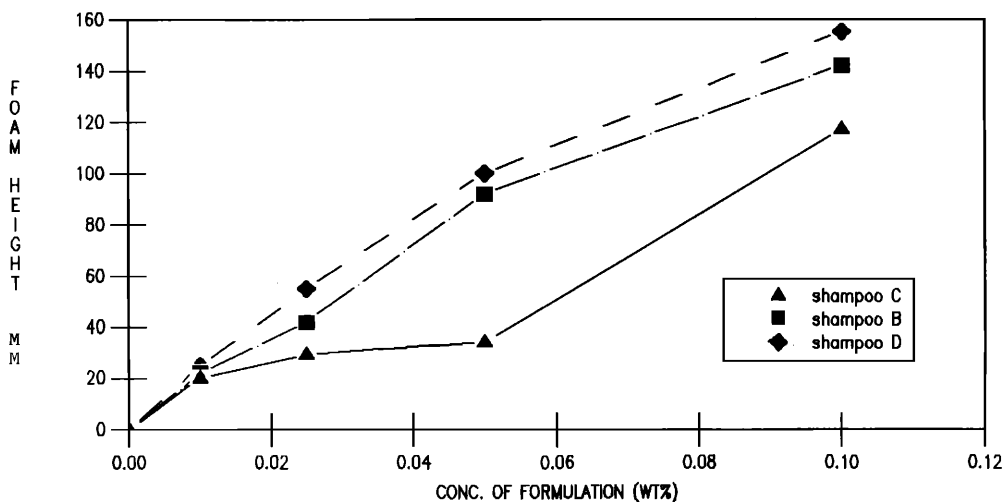


Figure 7. Foam height (T = 5 min). 50 ppm CaCO₃ in water.

of solubility of DDMAO under acidic conditions prevented a comparison at acidic pH. Furthermore, DDMAO was judged to suppress foam to a greater extent than SDMAO under the test conditions.

AMINE OXIDE SOLUTION RINSES

A comparison of DDMAO with SDMAO was made using simple solutions of these amine oxides in water or alcohol. Stearalkonium chloride was also included in this evaluation. Due to the total insolubility of DDMAO under acidic conditions, the role of pH was not examined. The effects of co-conditioner ingredients like long-chain alcohols or silicones were also not examined.

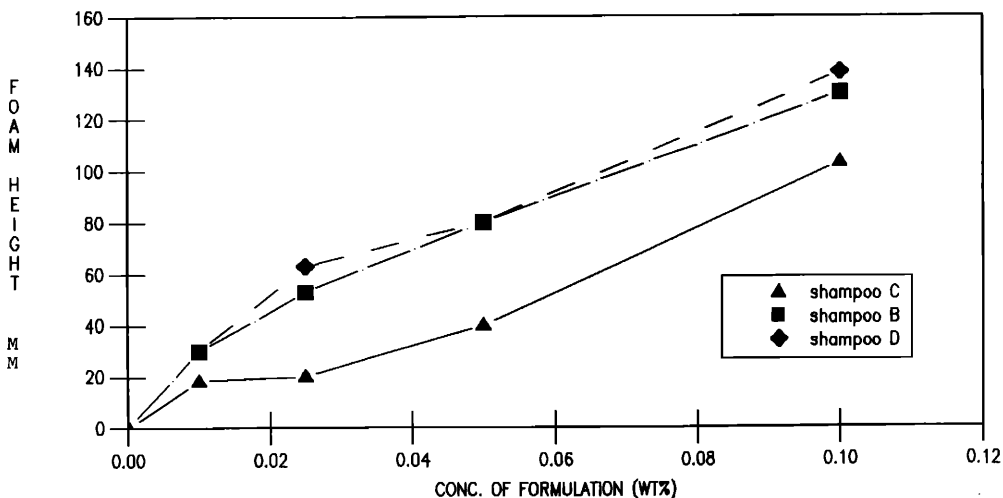


Figure 8. Foam height (T = 0 min). 150 ppm CaCO₃ in water.

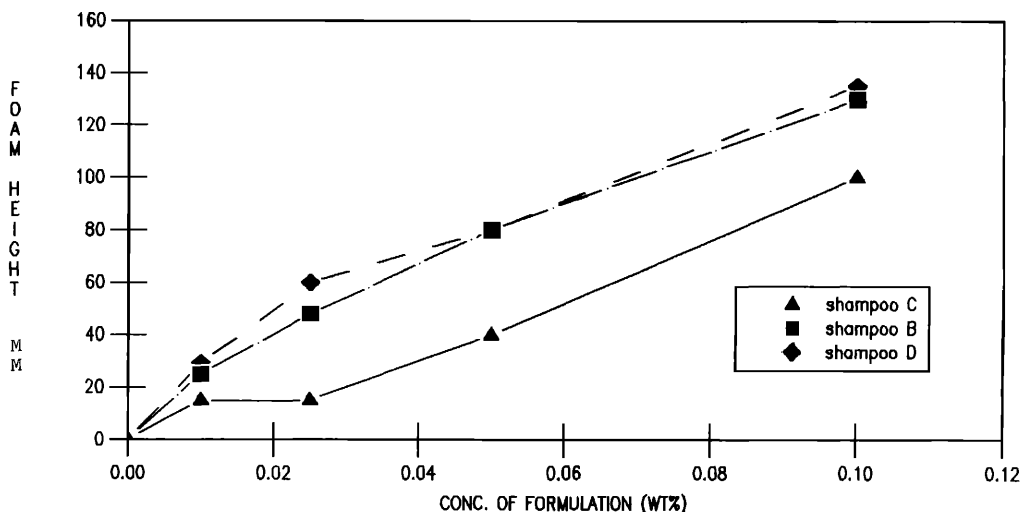


Figure 9. Foam height ($T = 5$ min). 150 ppm CaCO_3 in water.

As Table VIII shows, solutions E, F, and G each contained 3% of one of the three amine-based ingredients. Table IX contains conditioning-related property test data on untangling, comb drag, flyaway, and overall appearance. Rinse F (3% SDMAO) was more effective than rinse E (3% stearylalkonium chloride) in untangling activity and flyaway control. Rinse G, which contained 3% DDMAO, gave an extremely oily feel to the hair tress. The results parallel those in the above-described conditioning shampoo study which reveal the desirability of using DDMAO at a lower concentration than would be utilized for SDMAO near neutral pH. However, it is conceivable that the use of acidic pH might obviate this desirability for DDMAO.

Solutions containing lower concentrations (1.5, 0.5, and 0.1%) of each amine derivative were also evaluated, providing similar results. At 0.1% DDMAO no oily feel to the hair was noted.

Table VII
Foaming Behavior of Shampoos Containing Amine Oxides

Formulation	Conc. (wt %)	Foam height (mm)					
		T = 0 min			T = 5 min		
		No soil	Soil	% Foam retained	No soil	Soil	% Foam retained
B	0.05	100	30	30	95	30	32
B	0.10	145	135	93	50	50	100
B	0.20	175	155	89	170	145	85
C	0.05	70	20	28	70	20	28
C	0.10	120	50	41	120	45	38
C	0.20	155	150	97	150	140	93
D	0.05	115	30	26	105	25	24
D	0.10	160	60	37	160	55	34
D	0.20	170	155	91	170	155	91

Table VIII
Solutions* Containing Amine Oxide/Cationic Ingredients

Component	Weight % (active basis)									
	E	F	G	H	I	J	K	L	M	N
Didecylmethylamine oxide	0	0	3.0	1.5	0.5	0.1	0	0	0	0
Stearyltrimethylamine oxide	0	3.0	0	0	0	0	1.5	0.5	0.1	0
Stearalkonium chloride	3.0	0	0	0	0	0	0	0	0	0
Ethanol	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Water	95.0	95.0	95.0	96.5	97.5	97.9	96.5	97.5	97.9	98.0

* pH = 6.9 (unadjusted).

CONCLUSIONS

The physical properties of DDMAO were found to be substantially different from the properties of the analogous SDMAO. Molecular modeling suggests that the increased steric hindrance around the N–O moiety of DDMAO is a possible explanation of this behavior.

The difference between the two compounds is also observed in the activity of these two amine oxides in both prototype shampoos and in skeleton rinses. In shampoo formulations, DDMAO was effective as a detangling agent at lower concentrations than SDMAO. However, shampoos containing SDMAO produced more foam than systems having a comparable amount of DDMAO. In rinses solutions, DDMAO was judged to be more effective in detangling and flyaway control than SDMAO and stearyltrimethylamine chloride. However, poor solubility of DDMAO at acidic pH prevented it from being examined under acidic conditions. Hair effects with co-conditioner ingredients like long-chain alcohols or with silicones were not examined.

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Table IX
Combing Behavior of Hair Treated With Solutions of Amine Oxides or Cationic

Solution	Wet comb		Dry comb		
	Strokes to untangle	Drag	Flyaway (cm)	Appearance	Feel
E	12	Slight	4.0	Curl retained	Soft
F	8	Slight	2.0	Curl retained	Soft
G	4	Slight	0.5	Wet, stiff, no curl	Oily
H	2	Slight	0.5	Wet, stiff, no curl	Oily
I	2	Slight	2.5	Wet, curl retained	Slightly sticky
J	2	Slight	3.0	Shiny, curl retained	Soft
K	6	Moderate	3.0	Shiny, curl retained	Soft
L	5	Moderate	4.0	Shiny, partial curl	Soft
M	6	Moderate	4.3	Frizzy	Less soft
N	8	Moderate	4.6	Frizzy	Coarse

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(b) The new compound gave satisfactory elemental analyses and spectral data consistent with its structure.
1H NMR (360 MHz, d₆-acetone) δ 0.87 (t, 6H), 1.32(br s, 20H), 1.37(br s, 8H), 1.88(m, 4H), 3.36(s, 3H), 3.58(m, 4H).
13C NMR (360 MHz, d₆-benzene) δ 14.3, 23.1, 23.8, 27.1, 29.9, 30.1, 32.4, 56.0, 67.8.
UV (1 wt % in EtOH) 270(sh), 275 nm.
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