

Equilibration Reaction of Silicone Fluids

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Silicone fluids are used in many cosmetics and personal care products. This article looks at the synthesis of silicone fluids and evaluates whether that process can be viewed as an equilibrium reaction.

Silicone Fluids

Silicone fluids are a class of compounds that have become known by a variety of names including silicone oils, dimethyl fluids, dimethyl polysiloxane, and polydimethyl siloxane. Silicone fluids have become an important class of materials over the years. These materials are unique in terms of chemistry when compared to hydrocarbon-based materials. While much has been learned about these compounds since they were developed in the 1940s, the available published

data remains somewhat limited related to certain aspects of the chemistry.

Silicone fluids are sold by their viscosity. Commercial products range in viscosity from 50 centistokes (cst) to 1,000,000 cst. Silicone fluids are divided into several classes based upon viscosity. The first is regular viscosity fluids (RVF) that include viscosities ranging from 50 cst to 1,000 cst. The second is the high viscosity fluids (HVF), that include viscosities ranging from 10,000 cst to 60,000 cst and the third is the ultra high viscosity fluids (UHF) which exceed 60,000 cst. If the product is not made by blending two different viscosity fluids, the viscosity is related to molecular weight. Silicone fluids conform to the structure shown in Figure 1. The viscosity allows for an approximate calculation of the value of "n" as shown in Table 1.

Silicone polymers have become an increasingly important component of personal care products. Table 2 lists some of the functions and use levels of silicone fluids in personal care products.

Synthesis

Silicone fluids are synthesized by the equilibration reaction of hexamethyl disiloxane (MM) and cyclomethicone. D-4 is the most common type of cyclomethicone. Typical of the synthesis of fluids is the reaction in which one MM is reacted with D-4 to make MD_nM, a simple silicone fluid.

The reaction can be run with either

Key words

polymers, silicone fluids, synthesis, equilibration reaction, polydimethyl siloxane, cyclomethicone, viscosity

Abstract

Silicone compounds resemble organic compounds in their ability to make derivatives, but they are fundamentally different because they are equilibrium products. The nature of the equilibrium and the composition of the equilibrium mixture are the key factors. This is important because cyclic compounds are undesirable in personal care products.

Table 1. The "n" value for selected silicone fluids

Approximate Viscosity at 25°C (Centistokes)	Approximate molecular weight	"n" Value
5	800	9
50	3,780	53
100	6,000	85
200	9,430	127
350	13,650	182
500	17,350	230
1,000	28,000	376
10,000	67,700	910
60,000	116,500	1,570
100,000	139,050	1,875

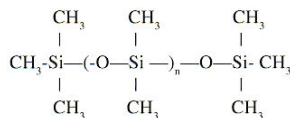


Figure 1. Structure of silicone fluids

Table 2. Cosmetic usage of silicone fluids¹

Product type	Desired effect	Use level
Skin lotion	Desoaping	0.1%
	Rub-out	0.1 – 0.5%
	Protection	1 – 30%
	Feel	0.5 – 2%
Skin cleaner	Lubricity	0.1 – 0.5%
	Wetting	0.1%
Antiperspirant	Anti-whitening	0.5 – 2%
	Detackification	0.5 – 2%
Preshave lotion	Lubricity	0.5 – 2%
Aftershave lotion	Feel	0.5 – 2%
Makeup	Water resistance	1 – 5%
Shaving cream	Reduce razor drag	0.5 – 2%

an acid or a base catalyst. In one method, the reaction is conducted at room temperature for 12 hours with sulfuric acid as a catalyst, resulting in a mixture of silicone fluid and free D-4. If the catalyst is neutralized and the cyclic is stripped off, a stable fluid results. If the catalyst is not neutralized during stripping, the fluid will degrade.^{2,3}

The equilibration process is critical not only to the production of stable

silicone fluids, but also as a means of introducing functional groups into the polymer. This is done using a process called hydrosilylation, a process used to make organofunctional silicone compounds. The difference between the equilibration used to make fluids and equilibration used to make organo-functional fluids is the latter includes silanic hydrogen compounds into the reaction.

It is also quite interesting to note that a "finished silicone fluid" may be placed in contact with additional D-4 and catalyst and re-equilibrated to make a higher viscosity fluid. Conversely, a "finished silicone fluid" may be re-equilibrated with additional MM and catalyst to make a lower viscosity fluid. Finally, silicone rubber may be partially decomposed into MM and D-4 via stripping of the product in the presence of catalyst. This property of silicone polymers makes them decidedly different from organic compounds.⁴

Equilibration

It is thought that silicone polymers form in equilibrium with their reactants. If true, the equilibration mixture can be pushed towards the reactant side of the equation under the correct circumstances. The reactants are $\text{Si}(\text{CH}_3)_2\text{-O-Si}(\text{CH}_3)_2$ (MM) and $\text{-(Si}(\text{CH}_3)_2\text{-O)}_n$ or D-4. Because D-4 is an eight-membered ring, having alternate silicon and oxygen atoms, its reaction with MM gives linear polymers in the presence of MM and catalyst. The process is referred to as ring opening. To be a true equilibrium reaction when MM is added to an already existing linear polymer, in the presence of catalyst, one might expect to get the equilibrium mixture of D-4 and a smaller linear molecule. If an excess of MM is combined with a linear polymer chain, in the presence of catalyst, one might expect to get a different polymer consuming the MM. Little is published on the nature of the reversibility of the reaction known as equilibration.

In order to evaluate the nature of the equilibrium, a study was undertaken which included:

1. Reacting MM and D-4 and building it up to a viscosity of 350 cst, and also to 1,000 cst;
2. Adding MM to break down the 1,000 cst fluid made in step 1 and also to break down a commercially obtained 1,000 cst fluid;
3. Neutralization of the catalyst;
4. Analysis via Gel Permeation Chromatography of the products to determine the linear polymer concentration and the concentration of D-4 found in each.

One objective is to determine if the composition of product made by the so-called "build up process" is the same as the composition made by the so-called "break down process". Specifically, the concentration of D-4 will be of major interest. One possibility is that there will be a comparable amount of D-4 present regardless of whether the process is build up or break down. This possibility will be observed if the process is truly an equilibrium. Another possibility is that since commercial 1,000 cst product is



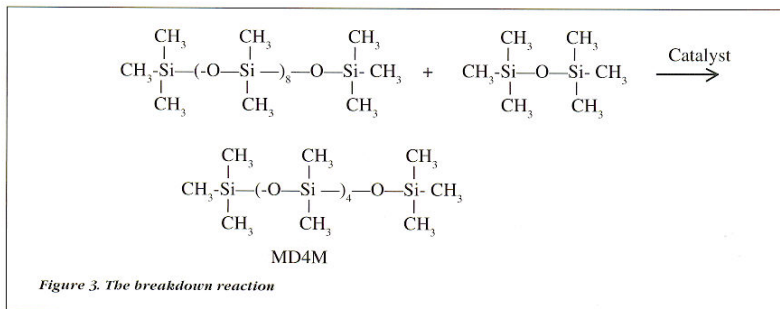
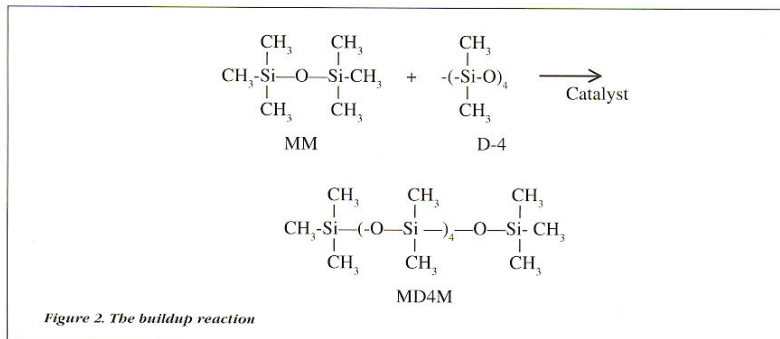
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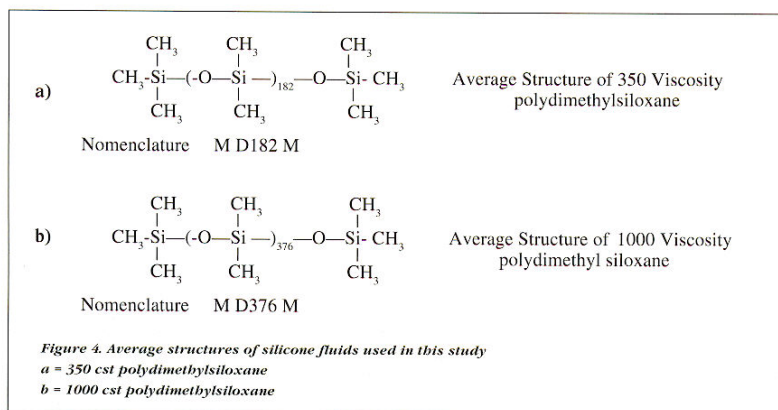
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stripped of D-4 after processing, the break down product may be very low in D-4.

The build up reaction is shown in Figure 2. The break down reaction is shown in Figure 3.

What is not clear from the literature is if the equilibrium mixture made by the build up process is the same as that of the break down product. If the reaction is a true equilibrium, it should not matter which path the reaction takes, but should be only determined by the ratio of reactants introduced. On the other hand it is possible when one breaks down a pre-existing silicone polymer, the silicone polymer might be the same but no D-4 would form. This would mean the reaction is not a true equilibrium.

The average structures of the two silicone fluids used in this study are shown in Figure 4.

If the silicone polymer made by the break down process results in no D-4, a cyclic free product might be possible by breaking down higher molecular weight polymers with MM. This is very important to the cosmetic industry because cyclic silicones are not desirable in cosmetic products. Many companies go through different synthesis to minimize the concentration of cyclic in their final product.

Methods and Materials

In our study, we used the five samples described in Table 3.

The equipment used for gel permeation chromatography analysis included an HPLC pump^a, a differential refractometer detector^b and a column heater module^c. The columns were Styagel HR 3, 1 and 0.5 in series with a flow rate of 1.0 mL/min, a mobile phase THF, a column temperature of 55°C and a detector temperature of 45°C.

Results

The results of the gel permeation chromatography analysis are presented in Table 4. The time shown in the table is the time needed to exit the column. The shorter the time the higher the molecular weight.

Discussion

Both the build up mechanism and the break down mechanism had a comparable quantity of cyclic products present. The break down from 1,000 cst to 350 cst had 5.29% cyclic silicones present before distillation, while the build up product had 4.65%. The commercial 350 cst product had less cyclic silicones present in it, at 1.58%. This is related to the degree of strip used after the catalyst is neutralized. It should be understood that there will be a certain amount of free D-4 in all fluids. Since many of the cosmetic products sold today have either acid or base present, it is not surprising to find some level of D-4 in products containing silicone fluids.

It is surprising however to see that a product that was built up, neutralized but not stripped, followed by a break down had twice as much cyclic silicone as the direct build up. The build up to 350 cst had 4.65% D-4 and the build up and break down had 10.39% D-4. It appears that in the case of this complex process there is a more complicated equilibration occurring, resulting in a different equilibration concentrations of product.

^a Waters HPLC Pump Model 515, manufactured by Waters and Associates, Milford, Massachusetts, USA

^b Waters Differential Refractometer Detector Model 410, manufactured by Waters and Associates

^c Waters Column Heater Module, manufactured by Waters and Associates

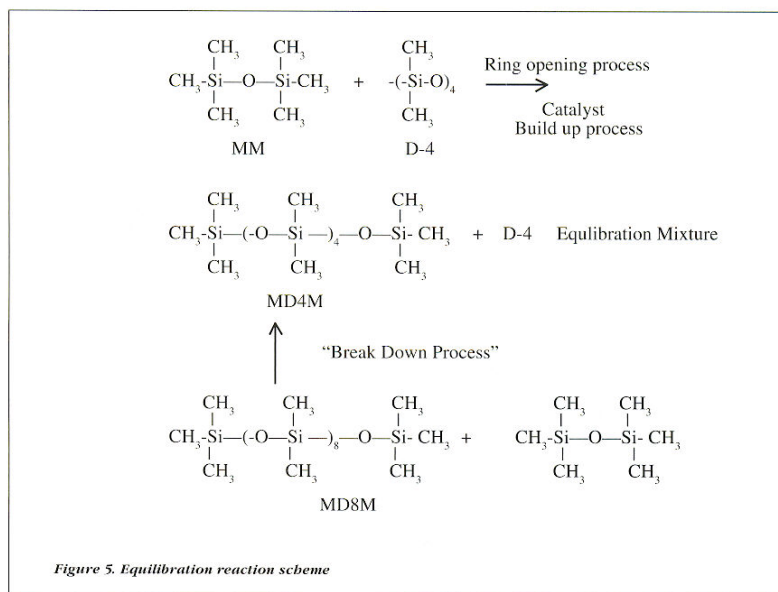


Table 3. Materials used in the study, showing composition in parts

A = 1000 cst (Build Up Process)
 B = 350 cst (Break Down Process) from commercial 1000 cst silicone fluid
 C = 1000 cst (Build Up Process) broken down to 350 cst
 D = 350 cst (Build Up Process)
 E = Commercial 350 cst product

Ingredient	A	B	C	D	E
Cyclomethicone	99.4		99.4	98.8	
Hexamethyl disiloxane	0.6	0.6	0.6	1.2	
Sulfuric acid	5.0	5.0	5.0	5.0	
Sodium bicarbonate	15.0	15.0	15.0	15.0	
Commercial 1,000 cst fluid		99.4			
Commercial 350 cst fluid					100.0

Procedures for samples A, C, D: Combine the amounts of hexamethyl disiloxane and cyclomethicone in a 400 mL flask. Stir well. Add sulfuric acid. Mix for 24 hours (under good agitation for sample A). Slowly add sodium bicarbonate. Foam will be encountered requiring venting of carbon dioxide. Filter.

Procedures for sample B: Combine the amounts of hexamethyl disiloxane and commercial 1,000 cst fluid in a 400 mL flask. Stir well. Add sulfuric acid. Mix for 24 hours. Slowly add sodium bicarbonate. Foam will be encountered requiring venting of carbon dioxide. Filter.

Table 4. Results of the gel permeation chromatography analysis, showing composition in % wt and time in minutes

A = 1000 cst (Build Up Process)
 B = 350 cst (Break Down Process) from commercial 1000 cst silicone fluid
 C = 1000 cst (Build Up Process) broken down to 350 cst
 D = 350 cst (Build Up Process)
 E = Commercial 350 cst product

Sample	Component	% Wt	Time
A	D-4	3.05	23.97
	Fluid	96.95	15.29
	Total	100.00	
B	D-4	5.29	23.38
	Fluid	94.71	15.57
	Total	100.00	
C	D-4	10.39	23.34
	Fluid	89.61	15.66
	Total	100.00	
D	D-4	4.65	23.45
	Fluid	95.35	15.64
	Total	100.00	
E	D-4	1.58	24.10
	Fluid	98.42	15.76
	Total	100.00	

Conclusions

Reference to the results in Table 4 suggests several interesting conclusions.

1. There are two different ways to make a 350 cst dimethyl polysiloxane - by build up (Sample D) or break down (Sample B). They result in essentially the same mixture of D-4 to polymer. Figure 5 shows the two reactions and the common product mixture.
2. Commercial 350 cst silicone is stripped to reduce the percentage of D-4 to under 2% (Sample E), from the original level of around 5% (Samples B and D).
3. The equilibrium mixture of dimethyl polysiloxane having a viscosity of 1,000 cst (Sample A) has a lower concentration of D-4 in the equilibrium mixture than the 350 cst product (Sample D). This too is not surprising since the 1,000 cst product has less D-4 in the original reaction.
4. The surprising result is Sample C, the product in which a commercial 350 cst dimethyl polysiloxane was built up to 1000 cst and then broken down to 350 cst. That sample had a very high level of D-4 - twice the expected amount based on Samples B and D.

The possibility of obtaining a truly D-4 free silicone fluid is quite small. Even if stripped D-4 levels are low, albeit non-zero, a re-equilibration can occur making new D-4. We believe it would be safe to say a truly D-4-free silicone fluid is not possible with this technology.

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