

MAGNETIC NANOFLUIDS STABILIZED WITH VARIOUS CHAIN LENGTH SURFACTANTS

L. VÉKÁS^{1,2}, DOINA BICA¹, OANA MARINICA²

¹Laboratory of Magnetic Fluids, Centre of Fundamental and Advanced Technical Research,
Romanian Academy – Timisoara Division

²National Center for Engineering of Systems with Complex Fluids,
University “Politehnica” Timisoara

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Abstract. Various chain length surfactants were used to prepare magnetic nanofluid samples with transformer oil and water carrier liquids. Magnetic and flow properties reveal the role of shorter chain length surfactants in the synthesis and colloidal stability of transformer oil and water based magnetic nanofluids with narrow size range magnetite nanoparticles.

Key words: magnetic nanofluid, magnetite nanoparticles, size distribution, lauric acid, myristic acid, dodecylbenzene sulphonic acid, oleic acid, sterical stabilization, magnetic properties, flow properties.

INTRODUCTION

Nano-sized particles (usually 3-15 nm particles of magnetite, maghemite or cobalt-ferrite) in a magnetic nanofluid are magnetically single domain and are in a permanent state of magnetization, *i.e.*, they have a magnetic dipole moment even in the absence of an applied magnetic field. Consequently, a strong long-range dipole-dipole interaction exists between individual particles, the result of which would be the agglomeration and subsequent sedimentation of particles unless a repulsive interaction is implemented to ensure the long-term colloidal stability of the nanofluid. The synthesis of magnetic nanofluids [1] is essentially a two-stage process, involving first the synthesis of magnetic nanoparticles, followed by the stabilization/dispersion of a prescribed amount of surface covered magnetic nanoparticles in various carrier liquids, to provide the most adequate magnetic nanofluids for experiments or applications envisaged. The increase of the particle volume fraction, *i.e.*, saturation magnetization, while keeping high the colloidal stability of the nanofluid, is one of the main requirements to be fulfilled.

Highly stable magnetic nanofluids exhibit reduced magnetoviscous effect [2] (up to 10%–20% increase of effective viscosity). Larger effects observed are due to weak colloidal stability of the magnetic nanofluids involved. Particle chaining and pronounced agglomerate formation due to van der Waals and magnetic dipolar interactions are prevented usually by sterical stabilization. The characteristics of the surfactant used, in particular the effective thickness of the resulted stabilizing layer determine the minimum interparticle distance and, consequently, the highest strength of the attractive forces. At the same time, the thickness of the surfactant layer together with the physical diameter of the particles, define their hydrodynamic diameter and limit the maximum magnetic volume fraction of the resulting magnetic nanofluid. Indeed, the greater the thickness of the surfactant layer, the greater the hydrodynamic volume fraction of particles, whose experimental upper limit is about 0.65 [3]. Consequently, the surfactant layer thickness and the mean particle size are among the key parameters in what concerns the colloidal stability and the upper limit of saturation magnetization of magnetic nanofluids.

In this work different chain length surfactants, dodecyl-benzenesulphonic acid (technical grade DBSA; approx. C16), lauric acid (LA; C12), myristic acid (MA; C14) and oleic acid (OA; C18), were used for coating magnetite nanoparticles in order to be dispersed in transformer oil (TR30), a weakly volatile and non-polar carrier, as well as in water, a highly polar inorganic solvent. In case the of transformer oil and, in general, of hydrocarbon carriers, rich experience was accumulated in using oleic acid, an excellent surfactant, to obtain magnetic nanofluids with hydrodynamic volume fraction and saturation magnetization close to the upper physical limits, $\Phi_h \sim 0.65$ and $M_s \sim 1100$ Gs, respectively (*e.g.* [3]). Stabilization/dispersion of magnetic nanoparticles in water implies a more complex mechanism, with double layer coating of particles. Stabilization of water based magnetic nanofluids at higher hydrodynamic volume fraction values, already over 0.1, proved to be a difficult task and involves combinations of surfactants of various chain lengths [4].

The aim of the experiments presented in this work was to evidence the influence of the surfactant chain length, *i.e.*, the surfactant layer thickness on the stabilization/dispersion process itself, as well as on the magnetic and in some cases, the magneto-rheological properties of samples.

SYNTHESIS OF MAGNETIC NANOFLUID SAMPLES

The chemical co-precipitation procedure, among the most efficient ones to produce nano-sized ferrite particles [1], was used to prepare magnetite particles to

be stably dispersed in non-polar and polar carriers. The experimental conditions established earlier for various carriers and surfactants [5, 6], such as mole fraction ratio for $\text{Fe}^{3+}/\text{Fe}^{2+}$, excess of alkali medium (NH_4OH), optimum temperature of precipitation and surfactant chemisorption, regime of further heating and mixing of reaction medium, as well as of particle surface covering and dispersion in the carrier used, were followed and adapted depending on the chain length of the surfactants.

TRANSFORMER OIL BASED SAMPLES

The procedure applied for the chemical synthesis of magnetic nanofluids with non-polar transformer oil carrier and LA, MA or OA as stabilizing layer, has the following main steps[5, 6]: co-precipitation ($\sim 80^\circ\text{C}$) of magnetite from aqueous solution of Fe^{3+} and Fe^{2+} ions in the presence of concentrated NH_4OH solution; sterical stabilization of subdomain magnetite nanoparticles (chemisorption of LA, MA or OA monolayer; $80\text{-}82^\circ\text{C}$); phase separation; magnetic decantation and repeated washing; extraction of monolayer covered magnetite nanoparticles; repeated flocculation and redispersion in light hydrocarbon (petroleum), elimination of excess surfactant; dispersion of monolayer coated magnetite nanoparticles in transformer oil carrier liquid. The resulted magnetic fluid samples due to mono-layer steric stabilization exhibit a high degree of colloidal stability and good flow properties even in a strong magnetic field, up to the limiting value of the hydrodynamic volume fraction of surface coated particles, of approx. 0.6.

The most frequently used surfactant, the oleic acid (OA), with 18 carbon atoms chain (C18) and a double bond, proved to be highly efficient in the stable dispersion of most of the ferrite nanoparticles resulted in the chemical synthesis procedure applied. The shorter chain length surfactants, LA (C12) and MA (C14), disperse only a part of the synthesized magnetite nanoparticles. Their stabilizing effect is quite different in comparison with oleic acid. The absence of a double bond, as well as the shorter chain length in the cases of LA and MA, both reduce the efficiency of particle dispersion, which becomes *size selective*, as will be shown in the paper. The shorter chain length surfactants LA and MA ensure stable dispersion only for the fraction of smaller particles and also reduce the poly-disperse character of the colloid [7], resulting in medium and high magnetization transformer oil based samples with narrow size range magnetite nanoparticles.

WATER BASED SAMPLES

Preparation of stable water based magnetic nanofluids is of renewed interest nowadays due especially to biomedical applications [8]. Double layer steric and

electrostatic (combined) stabilization of magnetic nanoparticles in water carrier proved to be efficient when colloidal stability had to be ensured for relatively large values (over 0.10) of the physical particle volume fraction Φ_p [9, 10].

Combinations of surfactants with different chain lengths were used, such as DBSA+DBSA, LA+LA, MA+MA, LA+DBSA, MA+DBSA. The quantity of surfactant added to 1 g of precipitate varied between 0.3÷0.5 g. The details of stabilization/dispersion of magnetite nanoparticles in water carrier to obtain stable magnetic fluids, such as pH and temperature, elimination of excess surfactant, depend on the surfactant combination. A thorough discussion of the stabilization mechanism of magnetite nanoparticles in water based systems may be found in [11].

RESULTS AND DISCUSSION

To evaluate the influence of various surfactant layers, the full magnetization curves of transformer oil (Fig. 1) and water (Fig. 2) based samples were determined using a vibrating sample magnetometer (VSM 880, DMS/ADE Technologies, USA). The overall view of $M/M_s = f(H)$ curves already denote the effect of the surfactant chain length, especially in the case of non-polar transformer oil based samples. The shorter the chain length of the surfactant, the lower the initial susceptibility of the sample. For a more detailed analysis of the magnetization curves, the ideal Langevin approximation of a mono-disperse (D^*) magnetic colloid and the Langevin type $M = M(H)$ dependence with log-normal particle size distribution were considered, as given in [12].

For a mono-disperse colloid, according to the Langevin approximation, the diameter of the magnetite nanoparticles is given by

$$D_m^* = \left(\frac{18\chi_i k_B T}{\mu_0 \pi M_d M_s} \right)^{1/3} \quad (1)$$

where: χ_i – the initial susceptibility; k_B – Boltzmann constant; T – absolute temperature; μ_0 – magnetic permeability of vacuum; $M_d = 4.46 \times 10^5$ A/m – saturation magnetization of magnetite; M_s – saturation magnetization of the magnetic fluid.

Taking into account the poly-disperse character of the magnetic colloid samples, D^* is actually the mean magnetic diameter of the larger size fraction of dispersed nanoparticles.

Considering log-normal size distribution of magnetic nanoparticles, according to [12], the parameters of the distribution in the Langevin approximation of the magnetization curves will be given by the following relations:

$$D_m = D_o \exp\left(\frac{S^2}{2}\right) \quad (2)$$

$$\sigma_m = D_o \exp\left(\frac{S^2}{2}\right) \left[\exp S^2 - 1\right]^{1/2} \quad (3)$$

where D_m – mean magnetic diameter; σ_m – standard deviation and

$$D_o^3 = \frac{6k_B T}{\mu_o \pi H_o M_d} \sqrt{\frac{M_s}{3\chi_i H_o}}$$

$$S = \frac{1}{3} \sqrt{\ln \frac{3\chi_i H_o}{M_s}}$$

$$n = \frac{\mu_o H_o M_s}{k_B T}$$

$$\ln(D_o) = \langle \ln(x) \rangle$$

x – magnetic diameter (D_m); S – deviation of $\ln(x)$ from $\ln(D_o)$.

H_o , χ_i and M_s are obtained from the $M = M(1/H)$ and $M = M(H)$ experimental curves.

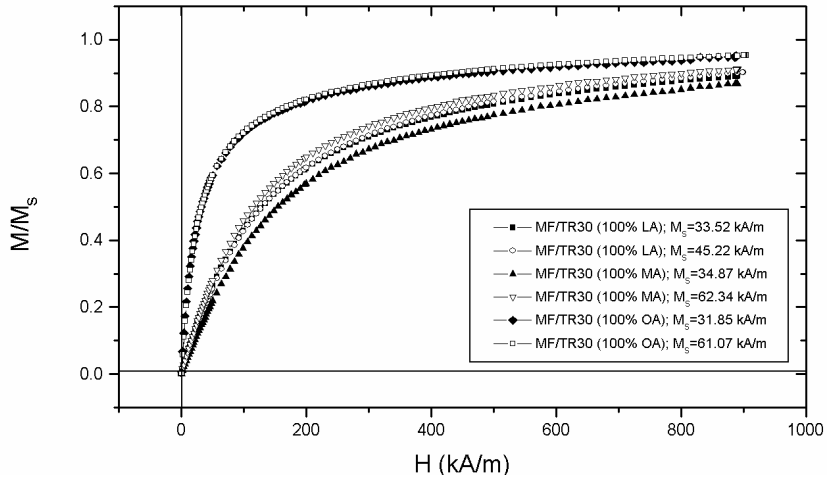


Fig. 1 – Non-dimensional full magnetization curves for transformer oil based magnetic nanofluids with various chain length surfactants (LA, MA and OA monolayers).

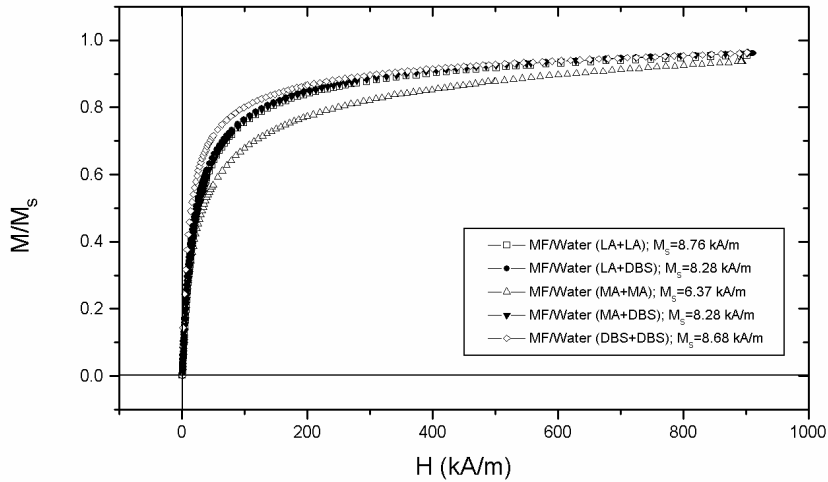


Fig. 2 – Non-dimensional full magnetization curves for water based magnetic nanofluids with magnetite nanoparticles stabilized with double layer of surfactants with various chain lengths (LA, MA, DBSA and their combinations).

The experimental saturation magnetization (M_s) and susceptibility (χ_i) values, together with the corresponding D^* , as well as D_m and σ_m values of the magnetic size distributions were obtained and given in Tables 1 and 2, for transformer oil and water based samples, respectively.

Table 1

Properties of transformer oil based magnetic nanofluid samples

No.	Sample	M_s (kA/m)	χ_i	D_m (nm)	σ_m (nm)	D^* (nm)
1.	Tr30 (LA/380)	33.52	0.17	5.0	2.3	6.0
2.	Tr30 (LA/510)	45.22	0.23	5.1	2.1	6.0
3.	Tr30 (MA/380)	34.87	0.15	4.7	2.1	5.6
4.	Tr30 (MA/713)	62.34	0.33	5.4	2.1	6.0
5.	Tr30 (OA/380)	31.85	0.73	6.1	4.6	9.9
6.	Tr30 (OA/730)	61.07	1.25	6.5	4.4	9.5

Table 2

Properties of water based magnetic nanofluid samples

No.	Sample	M_s (kA/m)	χ_i	D_m (nm)	σ_m (nm)	D^* (nm)
1.	Water (LA+LA)	8.76	0.23	6.2	5.0	10.3
2.	Water (LA+DBS)	8.28	0.23	6.4	5.0	10.5
3.	Water (MA+MA)	6.37	0.21	4.9	5.0	11.1
4.	Water (MA+DBS)	8.28	0.22	6.8	5.0	10.4
5.	Water (DBS+DBS)	8.68	0.35	6.5	5.6	11.9

Data given in Table 1 reveal the influence of coating thickness on the size of the dispersed particles. As expected, the shorter chain length LA and MA surfactants select out and stably disperse only the smaller size magnetite particles in the non-polar solvent transformer oil, while OA coating ensures the dispersion of practically the whole size range of magnetite nanoparticles resulted in the synthesis. Consequently, the mean magnetic size of LA or MA coated particles, approx. 5.0 nm, is less than the mean magnetic diameter of the OA covered ones, of about 6.1 nm. The influence of the thickness of surface coating is more evident in the case standard deviation, which is about 2.0-2.3 nm for LA or MA surfacted particles, in comparison with about 4.6 nm for the OA coated ones. The size selective dispersion of the magnetite particles is also well illustrated by the D^* values, which are significantly less in the case of LA or MA stabilized samples than for the OA stabilized one, which denotes that the shorter chain length surfactants ensure the stabilization/dispersion only of the smaller size particles.

In the case of water based samples the influence of the surfactant chain length is not so evident. Only the dodecylbenzenesulphonic acid double layer (DBSA+DBSA) covered magnetite particles have somewhat greater magnetic size than that resulted for the other samples. The water based samples, however, have several times larger magnetic susceptibility values than the stable transformer oil samples would have at the same particle concentration, *i.e.*, 0.2-0.3 vs. 0.04. These are due to agglomerates existing in water based samples, which behave as large particles and increase the apparent mean magnetic size of dispersed particles. Also, the standard deviation σ is clearly greater for water based samples, in comparison with those with transformer oil carrier and seems to be not influenced by the combinations of surfactants used.

For the transformer oil samples the magnetic field induced changes of the flow properties were investigated using a MCR type PHYSICA rheometer, with plate-plate type MR cell.

The shear stress vs. shear rate and effective viscosity vs. shear rate curves, under the influence of applied magnetic field are given in Figs. 3ab and 4ab for two samples, one with MA (sample 4, Table 1) and the other with OA (sample 6, Table 1) coated magnetite nanoparticles, respectively. Both samples have large saturation magnetization, practically the same, of about 60 kA/m (Table 1). However, there are important differences in the flow behavior of the samples. The OA stabilized sample, with larger particle size distribution, has a much lower viscosity (~ 0.1 Pa.s) than the MA stabilized one (~ 0.7 Pa.s), with narrower size distribution.

The magnetorheological effect, $\Delta\eta/\eta_0$, is relatively large for the OA stabilized sample (approx. 30%), in comparison with the MA stabilized one (less than 10%). This evidences the significant influence of the fraction of larger sized particles present in the OA stabilized sample on its flow behavior in magnetic field. At the same time, the effective viscosity of the MA stabilized magnetic fluid is about one order of magnitude larger than that of the OA stabilized sample, due to the relatively higher hydrodynamic volume fraction of smaller and narrower size range particles, at the same overall magnetic volume content.

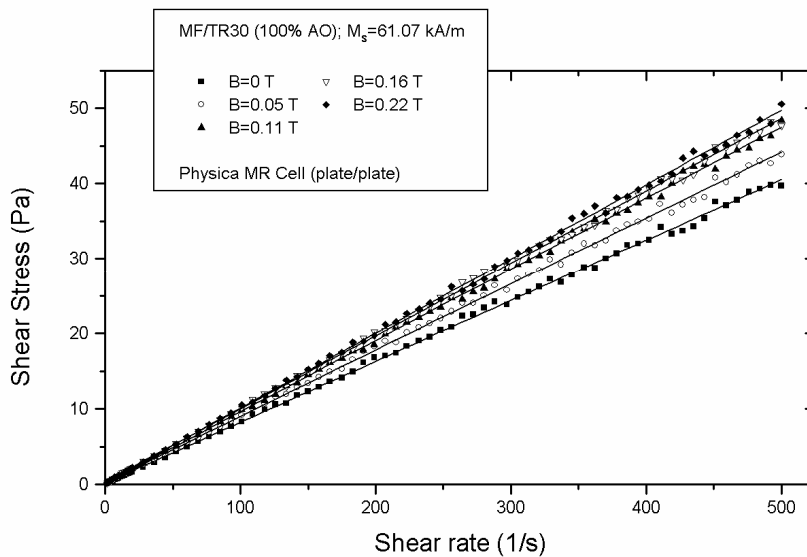


Fig. 3a – Flow curves under the influence of applied magnetic field for OA stabilized transformer oil based sample ($M_s = 61.07$ kA/m).

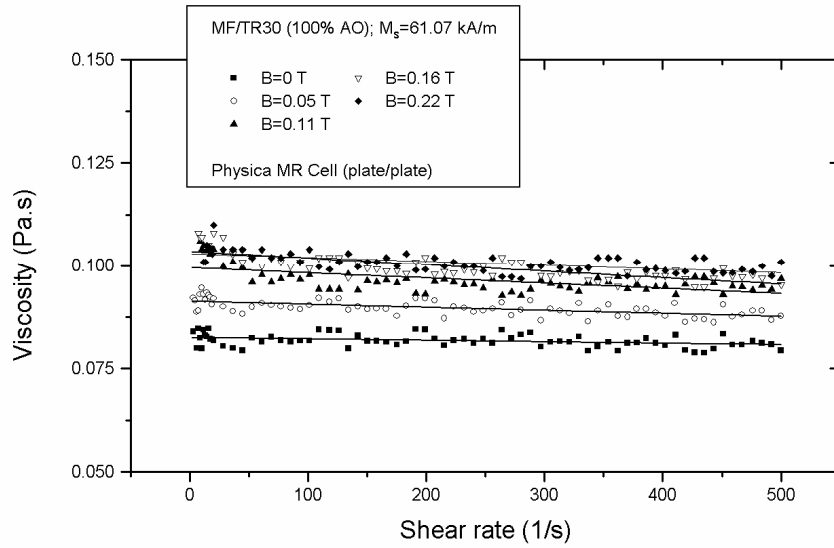


Fig. 3b – Effective viscosity vs. shear rate under the influence of the applied magnetic field for OA stabilized transformer oil based sample ($M_s = 61.07$ kA/m).

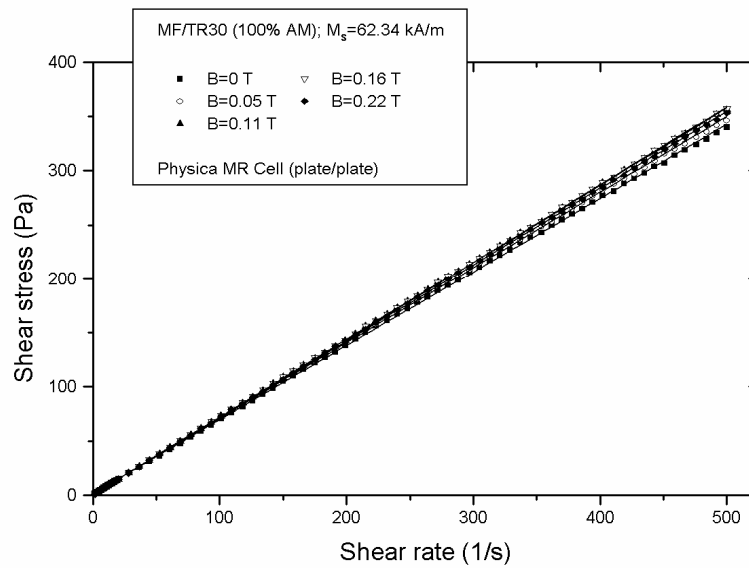


Fig. 4a – Flow curves under the influence of the applied magnetic field for MA stabilized transformer oil based sample ($M_s = 62.34$ kA/m).

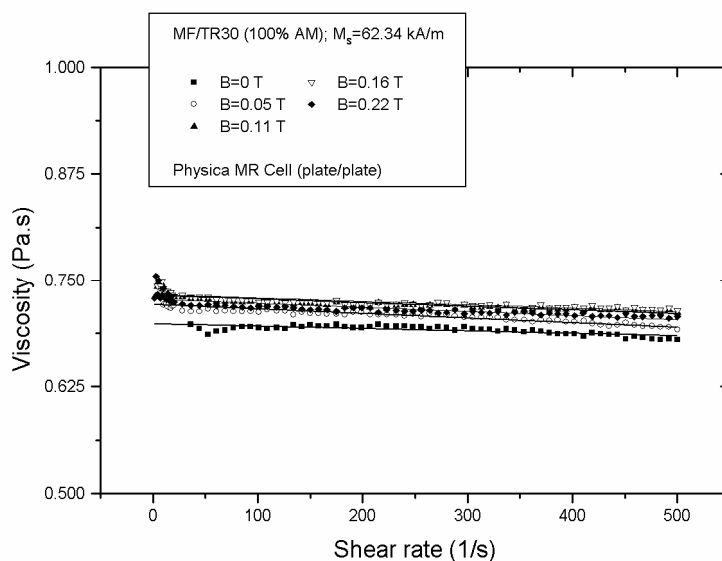


Fig. 4b – Effective viscosity vs. shear rate under the influence of the applied magnetic field for MA stabilized transformer oil based sample ($M_s = 62.34$ kA/m).

CONCLUSIONS

The use of various chain length surfactants in dispersing magnetite nanoparticles in non-polar hydrocarbon carrier, in particular transformer oil, allowed to tailor the thickness of the stabilizing layer, with significant influence on the magnetization curves and on the magnitude of the magnetoviscous effect. Shorter chain length LA and MA surfactants disperse only the lower dimensional fraction of the magnetite nanoparticles resulted in the chemical co-precipitation process. Medium and high magnetization LA and MA stabilized the transformer oil based samples resulted, with distinguished magnetic and flow properties. The initial magnetic susceptibility and relative increase of the effective viscosity in the external magnetic field are significantly lower than those observed for samples stabilized with longer chain length OA surfactant, which ensure the practically the dispersion of the whole dimensional range of magnetite nanoparticles resulted in the synthesis.

Water based magnetic nanofluids are in many respects a special category of magnetic fluids, mainly due to particularities of stabilization mechanisms and structural organization in various external conditions, in comparison with magnetic fluids on organic polar carriers, such as pentanol. Colloidal stability and fraction of large agglomerates are strongly dependent on the nature of the surfactant double

layer covering of magnetite nanoparticles. Short chain length surfactants, in particular LA+LA and MA+MA double layer coating of magnetite nanoparticles proved to ensure high colloidal stability of nanofluid samples, but these combinations of surfactants are less efficient in dispersing the whole dimensional range of nanoparticles resulted in the synthesis process.

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