

CHAPTER III EXPERIMENTAL

3.1 Materials

The chemicals used for the wax deposition experiments were all purchased from Sigma-Aldrich and are listed in Table 3.1. C₃₆, C₃₂, C₂₈, and C₂₄ were selected for the experiments because they can be used to prepare both cocrystallized and independently crystallized systems at reasonable temperatures. Dodecane is used as the solvent because the solubility data for these n-alkanes in dodecane are available, and it has a reasonably low vaporization rate at the experimental conditions being used. Stearic acid is selected as an additive in wax system because it has a cloud point (at 4 wt % concentration) close to C₃₂ (at 4 wt % concentration), which indicates the potential of interfering with the deposition mechanism of C₃₂ and C₃₆ (Senra, 2006). Heptane is used as a diluent for wax composition analysis to dissolve the deposit from the coldfinger into a homogeneous solution.

Table 3.1 Table of chemicals for wax deposition experiments

Chemical name	Formula	Purity (%)
Hexatriacontane	C ₃₆ H ₇₄	98
Dotriacontane	C ₃₂ H ₆₆	97
Octacosane	C ₂₈ H ₅₈	99
Stearic acid (Str)	CH ₃ (CH ₂) ₁₆ COOH	97
Tetracosane	C ₂₄ H ₅₀	99
Dodecane	C ₁₂ H ₂₆	99+
Heptane	C ₇ H ₁₆	99+

All systems analyzed in this study are listed in Table 3.2. Monodisperse systems are used as the base case for further comparison.

Table 3.2 Wax deposition systems studied: dodecane is used as the solvent and % represent mass % in solution

Monodisperse systems	Binary systems	Ternary system
4% C_{36}	4% C_{36} 4% C_{32}	4% C_{36} 4% C_{32} 4% C_{28}
4% C_{32}	4% C_{36} 4% C_{28}	
4% C_{28}	4% C_{32} 4% C_{28}	
4%Str	4% C_{32} 4% C_{24}	
	4% C_{36} 4%Str	
	4% C_{36} 2%Str	
	4% C_{36} 1%Str	
	4% C_{32} 4%Str	
	4% C_{32} 2%Str	
	4% C_{32} 1%Str	

3.2 Equipment

The equipment used in this study is a coldfinger apparatus to simulate wax deposition and a gas chromatograph to analyze the deposit composition. The coldfinger apparatus consists of a hollow metal probe with coolant passing through it, a 250 ml glass cylinder with a hollow jacket with hot water passing through it to control the bulk fluid temperature, two constant temperature baths (Brookfield EX-200 and Neslab RTE-111), a magnetic stir bar with a diameter of 0.92 cm and length of 3.77 cm, and a magnetic stirrer (Corning PC-410D) as shown in Figure 3.1. The metal probe outer diameter is 0.94 cm and the inner diameter of the coldfinger cylinder is 6.46 cm. The gas chromatograph (GC) used in this work is the Agilent Technologies 6890N GC.

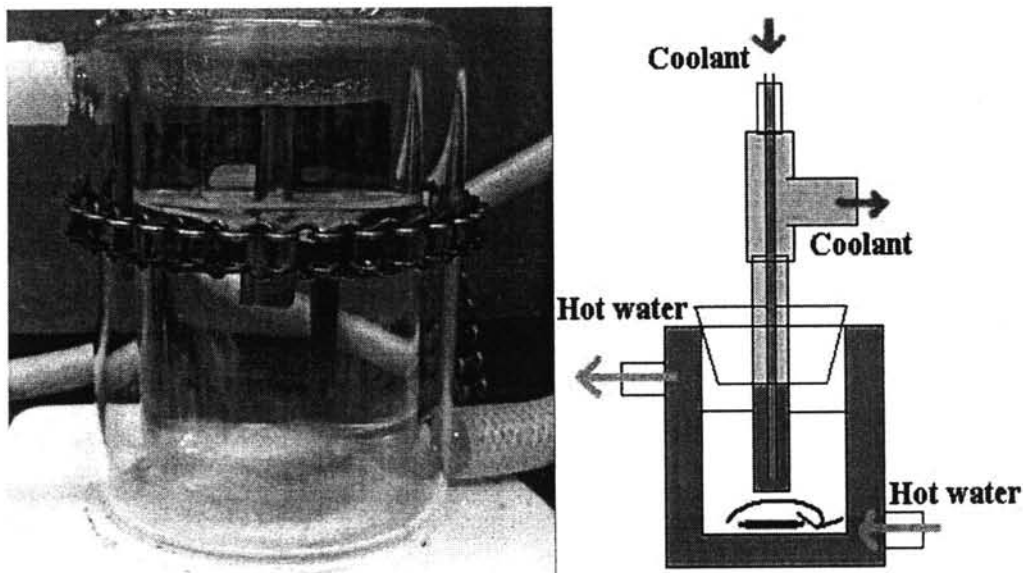


Figure 3.1 Picture and schematic of the coldfinger apparatus.

3.3 Experimental Procedures

3.3.1 Cloud Point Measurement

To determine the cloud points of the systems shown in Table 3.2, a constant temperature bath was used. The initial temperature is set to a temperature above the sample cloud point. The samples are held at the initial temperature for 30 minutes to allow the system to equilibrate. The sample is then cooled down slowly and checked visually for clouding after the systems held for 30 minutes. If the sample has not clouded, the aforementioned process is repeated until visible clouding is seen.

3.3.2 Coldfinger Experiment

The coldfinger apparatus consists of two major parts, a metal like “finger” that has coolant circulating inside of it and a jar that is jacketed in order to provide a constant bulk temperature. The temperature gradient between the bulk fluid and the coldfinger will cause the formation of a deposit. The deposited wax will be scraped from the coldfinger after 6 hours, weighed and analyzed by GC. In the experiment, the solvent amount and length of coldfinger dipped into the hot oil must be the same to ensure the same contact length between the oil and coldfinger.

3.3.3 Deposit Composition Analysis

Gas chromatography is a tool that can be used to determine the composition of a sample. Each component can be identified and its presence can be measured by the size of its peak. The area under the peak is related to the amount of sample injected into GC. In order to find the proper composition, the GC needs to be calibrated. The calibration curves (as shown in Table 3.3) are fit to a linear equation with the intercept set to zero because no signal would occur when no material is present. Heptane is used to dissolve the sample before injecting into the GC to prevent the solution from solidifying in the syringe. The GC injections are completed numerous times in order to minimize the error from manual injection, which can be as much as 10%.

Table 3.3 GC calibration curve equation (y and x represent the peak area and actual concentration in ng/ μ l respectively)

Chemical name	Equation	R ²
Hexatriacontane	$y = 0.974 x$	0.966
Dotriacontane	$y = 1.152 x$	0.986
Octacosane	$y = 1.072 x$	0.989
Stearic acid	$y = 0.617 x$	0.983
Tetracosane	$y = 0.608 x$	0.988
Dodecane	$y = 0.675 x$	0.992

3.4 Experimental Procedure Development

For the deposition experiments, operating conditions and an experimental procedure needed to be developed to ensure reasonable consistency between trials. Three major issues can greatly impact reproducibility. The first issue is the experimental procedure in sampling the deposit for composition analysis. Initially, the middle part of the deposit was used to represent the whole deposit. However, it was shown (See Table 3.4) that deposit composition varies greatly with coldfinger

probe position. To account for this, the whole deposit was dissolved to determine the accurate composition of the deposit.

Table 3.4 Deposit composition of 4% C_{36} trial as a function of position. Operating conditions are coldfinger temperature of 5°C, bulk fluid temperature of 50°C, rotational speed of 60 rpm, and trial length of 68 hours 35 minutes

Deposit location	Composition of the deposit	
	% C_{36}	% C_{12}
Top	51.9	48.1
Middle	57.5	42.5
Bottom	56.6	43.4

A second issue is the drying of the deposit. In order to remove the excess oil from the deposit, the deposit was allowed to dry in the open. However, if the deposit is allowed to dry for too long, not only does the excess surface oil evaporate, but also some of the liquid trapped inside the deposit. To investigate the effect of drying, the deposit mass was measured at different drying durations. The result in Figure 3.2 shows that the deposit mass decreases by approximately 15% after 24 hours and by a factor of 2 after 7 days. GC analysis shows that the sample is pure C_{36} after 7 days. Therefore, the systems were not dried, but the excess surface oil was shaken off the deposit to minimize the amount of surface oil present on the deposit.

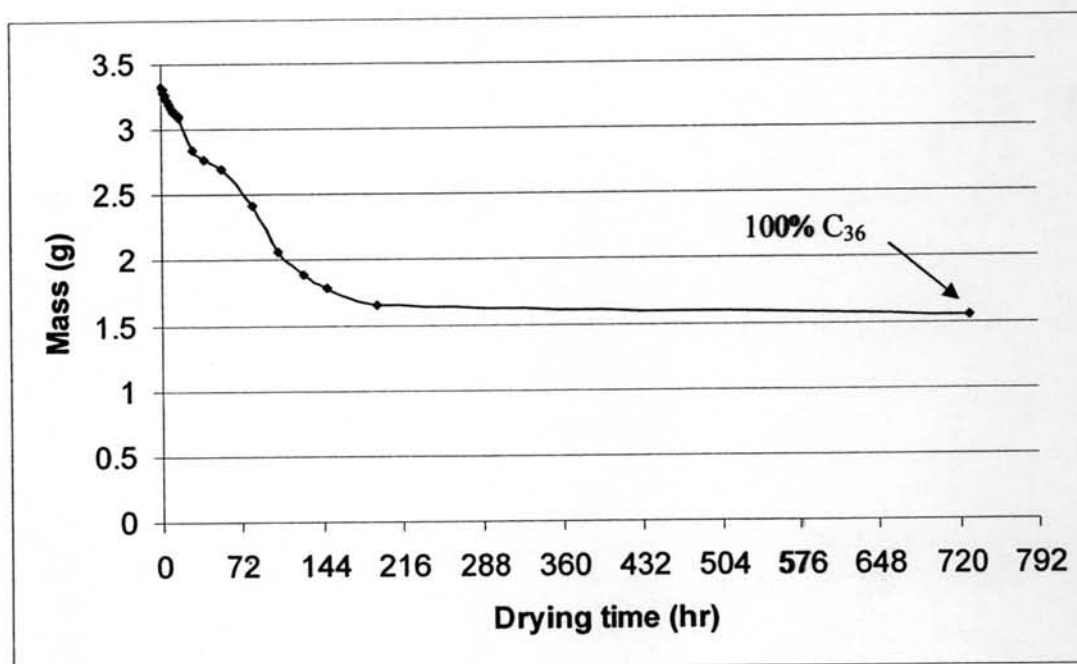


Figure 3.2 Deposit mass and composition of 4% C_{36} trial at various drying duration where coldfinger temperature is 5°C , bulk fluid temperature is 50°C , stir bar rotation speed is 60 rpm, and trial length is 22 hours 10 minutes.

A third issue that may impact reproducibility is the operating condition. Proper operating conditions are needed in order to produce a deposit that will adhere to the coldfinger probe and be consistent from trial to trial. The following section will discuss the development of satisfactory operating conditions.

3.5 Development of Coldfinger Operating Conditions

To determine proper coldfinger operating conditions, thermodynamic properties of systems must be known. The bulk temperature is set to 50°C to prevent wax precipitation in the bulk. The temperature of the coldfinger probe must be below the cloud point of all systems to ensure deposition. However, if it is too low, water from the air will condense onto the coldfinger probe after the experiment has finished, which can contaminate the deposit and lead to an error when weighing the deposit. Moreover, a lower temperature will cause deposits to form more rapidly and

become potentially too heavy to stick onto the coldfinger probe. If the mass is sufficiently high, it will fall from the probe because the adhesive force between the deposit and the probe is less than the gravitational force of the deposit. A case where the deposit falls from the coldfinger is seen in Figure 3.3.



Figure 3.3 Falling of the deposit.

Increasing the rotation of the stir bar speed can overcome the issue of falling deposits because it will provide higher shear to the system, reducing both deposit growth and deposit mass (Jennings and Weisfennig, 2005). However, if it rotates too fast, it will cause more turbulent flow, causing an inconsistent flow pattern. This flow pattern results in the oil surface being curved, causing a variation in the contact length. The optimum coldfinger temperature was determined to be 10°C and the optimum stir rate was found to be 340 rpm.

Another operating condition that was developed is the trial length. As discussed in Chapter 2, wax deposition occurs very fast initially, so if the deposit is collected in the fast deposition rate period, a significant deviation in deposit mass could occur. Thus, to avoid the fast deposition period, the deposit mass was found for a variety of times to determine the proper experiment run duration. These results are shown in Table 3.5.

Table 3.5 The deposit mass as a function of time to determine proper operating duration of 4% C_{36} where the operating condition are 10°C at coldfinger, 50°C at bulk fluid, and 340 rpm of stir bar rotation speed

Experiment duration	Deposit mass (g)
24 hours	1.24
12 hours	1.20
6 hours	1.24
15 seconds	0.29

Table 3.5 shows that 6 hours should be an acceptable trial time to run the apparatus, because it reduces the operating time while being sufficiently long to avoid the fast deposition period.