

# **SPREADING OF OIL-IN-WATER EMULSION ON MODEL SOLID SUBSTRATES**



By

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## **Certificate**

This is to certify that this dissertation entitled "Spreading behavior of oil in water emulsion on model solid substrates" submitted towards the partial fulfillment of the BS MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by Rupesh Kumar Xaxa at Unilever R&D, Bangalore, under the supervision of Mr. Sudipta Ghoshdastidar, Research Scientist, Skin Care Division during the academic year 2013-14.

Date:

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## **Declaration**

I, Rupesh Kumar Xaxa hereby declare that the matter embodied in the report entitled “Spreading behavior of oil in water emulsion on model solid substrates” are the results of the investigations carried out by me in the Skin Care Division, Unilever R&D, Bangalore under the supervision of Mr.Sudipta Ghoshdastidar and the same has not been submitted elsewhere for any other degree.

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## **LIST OF ABBREVIATIONS**

O/W	- Oil in water
W/O	- Water in oil
IPM	- Isopropyl Myristate
ISA	- Isostearic Acid
HLB	- Hydrophilic Lipophilic balance
PMMA	- Polymethyl Methacrylate
IFT	- Interfacial tension
DSA	- Drop Shape Analysis
UVB	- Ultra Violet B
MCX	- Ethyl hexyl methoxy cinnamate

## Abstract

In this report, we have studied the spreading behavior of cosmetic oils along with sunscreen on PMMA and Teflon. It was observed that most of the cosmetic oils used, spread completely on PMMA where as on Teflon it makes certain contact angle. Based on the spreading experiments, we found through Zisman plot that critical surface tension of Teflon is  $\sim 21$  mN/m. We found anomaly in spreading, in case of mixture of IPM and MCX and based on our finding, we concluded that not only surface tension but also viscosity of oil plays important role in spreading phenomenon. We also measured the IFT of pure oils with and without nonionic surfactant and in case of pure oils, lower IFT value is observed when the interaction happens through hydrogen bond interaction and higher IFT values are obtained when the interactions are van der waals in nature. Nonionic surfactant,  $C_{12}EO_7$  brings down the IFT values very significantly to  $\sim 0.5$  mN/m and we also measured the emulsion droplet size with various concentration of surfactant. It was observed that smaller droplet sizes were obtained at higher surfactant concentration. Spontaneous spreading of IPM emulsion with  $C_{12}EO_7$  as surfactant on glass and Teflon was performed. It was observed that in case of glass, precursor film first moves where as emulsion droplets are not spreading further and they are pinned. After a period of time, emulsion droplet coalesces and spreads completely. In case of Teflon, we found that movement of precursor film was very slow and the distance travelled by the film was less compared to glass.

## 1. Introduction

Emulsions are thermodynamically unstable system of two immiscible liquids, usually oil and water kinetically stabilized by surfactant through interfacial tension reduction. Spreading of emulsion on solid surface plays very important role in delivering the functional benefits in the area of cosmetics, paint industry, agricultural spray and food industry [1, 2]. Our interest in emulsions is primary in the context of cosmetic formulations. Emulsions are one of the major building blocks in cosmetic skin care products which are used to deliver functional benefits like moisturization, sun care, anti-aging, etc. Emulsions can be majorly classified as oil-in-water (O/W) and water-in-oil (W/O) emulsions, though both the types of emulsion are widely used as delivery vehicles, O/W emulsion is prominent. Both are used in skin care formulations with the former being more predominant. These emulsion based products when applied on skin, water evaporates over a period of time leaving behind the oil phase which comprises of cosmetic oils, emollients, functional ingredients and emulsifiers. So the spreading behavior of this oil phase ultimately decides the final efficacy of the formulation. Majority of the sunscreens currently used are oil soluble, hence spreading of oil phase present in the emulsion plays an important role in delivering various functional benefits. Thus the focus of this work will be on understanding the spreading of emulsion of pure oil and mixture of oils and sunscreen.

In the following section, we briefly explain fundamental aspects of spreading of liquids on solid substrates. This learning will help us in understanding of emulsion spreading phenomenon better. We begin the discussion by explaining the relationship between surface tension, contact angle and interfacial tension. These relationships form the basis of thermodynamics of spontaneous spreading of a liquid drop on solid surface. Spreading of pure liquids on solid substrate is well studied [3-8, 20]. Surface tension is defined as the minimum energy required for creating a unit surface area in vacuum. Surface tension especially critical surface tension ( $\gamma_c$ ) is one of the important parameter in deciding the spreading behavior of liquid on any substrate. Contact angle can be defined as the angle that a liquid drop makes on a solid surface. The concept of contact angle is represented in the *figure 1*. The contact angle and surface tension can be

related by the Young's equation (equation 1), where  $\gamma^S$ ,  $\gamma^L$ ,  $\gamma^{SL}$  are solid-air, liquid-air and solid-liquid interfacial tensions respectively. Interfacial tension can be defined as the minimum energy required for creating a unit surface area at the interface between the two immiscible liquids.

$$\gamma^S = \gamma^L \cdot \cos\theta + \gamma^{SL} \quad (1)$$

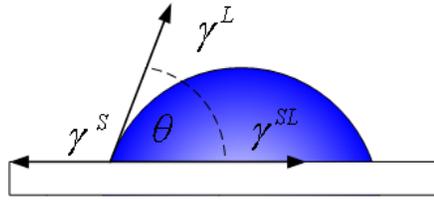


Figure 1: Schematic representation of Young's equation.

Surface and interfacial tensions are expressed either in terms of force unit (mN/m) or energy unit ( $\text{mJ/m}^2$ ). The origin of surface/interfacial tension is due the force imbalance of the molecules present at the interface where as the molecules present at the bulk are balanced. The quantum of the surface/interfacial tension is decided by the various inter-molecular forces of attraction. The spreading of a liquid on solid surface is determined by the spreading coefficient  $S$ , which is a manifestation of cohesive force of liquid and adhesive force between liquid and solid. This spreading coefficient can be expressed by the following equation,

$$S = \gamma^S - (\gamma^L + \gamma^{SL}) \quad (2)$$

If  $S$  is positive, the liquid completely spreads on the surface; in other words adhesive force out wins over the cohesive force of the liquid. On the other hand if the  $S$  is negative, liquid does not spread completely, and forms a droplet.

A brief literature review suggests that the reported work are majorly on spreading behavior of pure liquids [3-8], especially silicone fluids of different viscosity on hydrophilic and hydrophobic substrates and effect of precursor film on spreading of pure fluid [9,11,12,20]. Studies have been done understanding the spontaneous spreading

behavior of water-in-silicone emulsion on both hydrophobic and hydrophilic substrates [10, 11 and 19]. Role of precursor film in spreading W/Si emulsion was also investigated [9]. Recently the spreading behavior of cosmetic emulsion on human skin studied using instrumental technique and human sensorial perception was reported [13, 17, and 18]. Apart from the properties of the emulsion and pure liquids, the surface energy and microstructure of substrate plays very important role in deciding the spreading of the liquids [14, 15, and 21]. Human skin has critical surface tension value of 22-30 mN/m and it varies from one person to other [22]. Surface tension of oils used in cosmetics generally ranges from 18 to 35 mN/m [16]. Surface tension, viscosity and presence of surfactant (emulsifiers) decide the ultimate spreading of oil phase present in the emulsion. Our literature review suggest that spreading of pure cosmetic liquid and oil-in-water emulsions on surfaces with different surface energies is not well reported and hence there is a need for a systematic understanding of the same. In this study, we have focused on understanding the spreading behavior of pure cosmetic liquids and emulsions onto model solid surfaces.

## **2. Materials and Methods**

### **2.1 Materials**

Pure cosmetic oils Arlamol HD, IPM, Ceitol CC, Ceitol C5, Isostearic acid (trade name: Prisorine 3505) and Isostearyl alcohol (trade name: Prisorine 3515) were obtained from Croda chemicals. Parsol MCX (UVB sunscreen) and mineral oil (light liquid paraffin oil (LLPO)) were obtained from Unilever factories. Trade name and INCI name of these chemicals were provides in the *Appendix 1*. Fatty alcohol ethoxylate nonionic surfactants C<sub>12</sub>EO<sub>7</sub> obtained from galaxy surfactants and C<sub>12</sub>EO<sub>3</sub> was obtained from Surfachem international limited. Teflon substrate was purchased from local manufacturer whereas PMMA was purchased from Shoenberg, Germany. Standard microscopy grade glass substrate was purchased from Polar industrial corporation.

### **2.2 Choice of substrate**

Two model hydrophobic substrates were used for this study: Poly methyl methacrylate (PMMA) and Teflon. Spreading of a liquid happens on a solid substrate only when the

surface tension of liquid is less than the critical surface tension of solid. PMMA has surface energy (39 mN/m) value and it is widely used substrate for *in vitro* sun protection efficacy measurement because of its comparable surface energy with human skin. Majority of the cosmetic oils used for spreading experiment completely spreads on PMMA substrate and in order to understand the differential spreading behavior of different oils, we used Teflon (16-20 mN/m) substrate for further experiments.

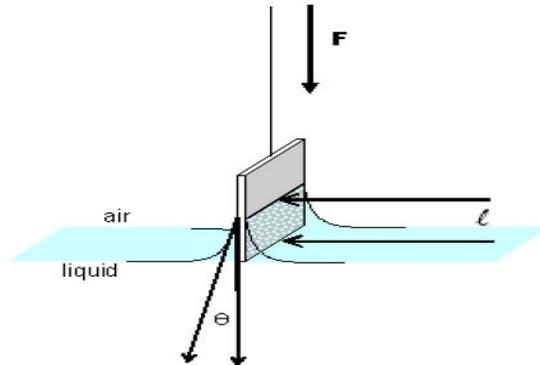
### **2.3 Measurement of Contact Angle**

The liquid whose contact angle to be measured was taken a Hamilton micrometer syringe and a drop was placed on the substrate carefully and change in contact angle was monitored over a period of 30 minutes. As these liquids have very low vapour pressure, will not evaporate during the 30 minutes of study. The contact angle of the liquid drop was measured using *Kruss Goniometer (G1023)* by the *Circle Drop* method. The recorded values were also validated with the *Dropsnake* plug-in of the Image J software, description of which is given in *Appendix 4*.

### **2.4 Measurement of surface tension and interfacial tension**

Surface tension of pure liquid and interfacial tension between oil and water without surfactant was measured by *Kruss K 12 Tensiometer* using Wilhelmy plate method. For measuring surface tension, a thin plate made up of platinum called Wilhelmy plate was used and the plate was cleaned well with acetone and also cleaned using burner flame. Then the plate was hung on metal connector which connects the plate to balance. The plate is then moved closer to the surface of the liquid and the liquid should not touch the surface of the plate. The force acting on the plate due to its wetting is measured by the tensiometer with the help of which it calculates the surface tension (*figure 2*). After every measurement, the beaker containing the liquid was washed well with surfactants and ethanol/acetone. Also surface tension of water was measured as a standard before measuring the next fluid to ensure the cleanliness of the plate as well as container. For measurement of interfacial tension between oils and water, first the platinum plate was inserted fully in the oil for calibration. After that, the light phase i.e. the oil was removed and the heavy phase was put in the beaker, the plate was dipped inside as instructed by

instrument and then the plate was covered with the light phase. Then the instrument measures the IFT.



*Figure 2: Schematic representation of Wilhelmy plate measurement*

## **2.5 Measurement of low interfacial tension**

Interfacial tension between oil and water in the presence of surfactant was measured using *Kruss Spinning Drop Tensiometer SITE 100* instrument. In this instrument, a capillary was horizontally fixed and filled with a bulk phase ( in our case it was surfactant solution in water) and a drop of light phase was inserted carefully in the same capillary using a syringe and the capillary is set for rotation (*figure 3*). The diameter of the drop changes once the angular acceleration changes and hence oil drop elongates. Once the length of drop ( $L$ ) is more than four times of diameter of the drop ( $d$ ), the IFT can be measured. The radius of the drop perpendicular to the axis of rotation depend on the density difference  $\Delta\rho$  of the two phases, angular frequency  $\omega$  of the rotation and interfacial tension  $\gamma$  between two phases. Thus with a given speed of rotation and known densities of two phases, the interfacial tension can be calculated using the following Vonnegut's equation:

$$\gamma = \frac{r^3 \cdot \omega^2 \cdot \Delta\rho}{4} \quad (3)$$

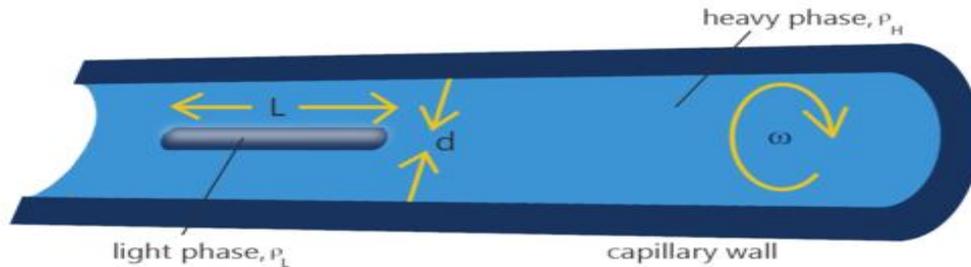


Figure 3: Schematic diagram of interfacial tension measurement using spinning drop tensiometer

## 2.6 Preparation of o/w emulsion

Oil in water emulsion was prepared using *IKA High Speed Homogenizer*. For making o/w emulsions, 10% oil, various concentrations of surfactant and water were taken in a plastic container (from Tarson) and mixed at a speed of 13,500 rpm for ten minutes. We all know that oil and water are immiscible with each other due to their high interfacial tension between them. In order to decrease the interfacial tension we add surfactant and the emulsifier molecules decrease the interfacial tension. These emulsifier molecules have a hydrophilic head and a hydrophobic tail. The hydrophilic group is attracted towards water while the hydrophobic tail is attracted towards oil. Due to this feature, the emulsifier molecule sits at the interface of oil and water and hence reduces the interfacial tension and produces kinetically stable emulsion. The schematic diagram of emulsion and surfactants are given in the *figure 4*.

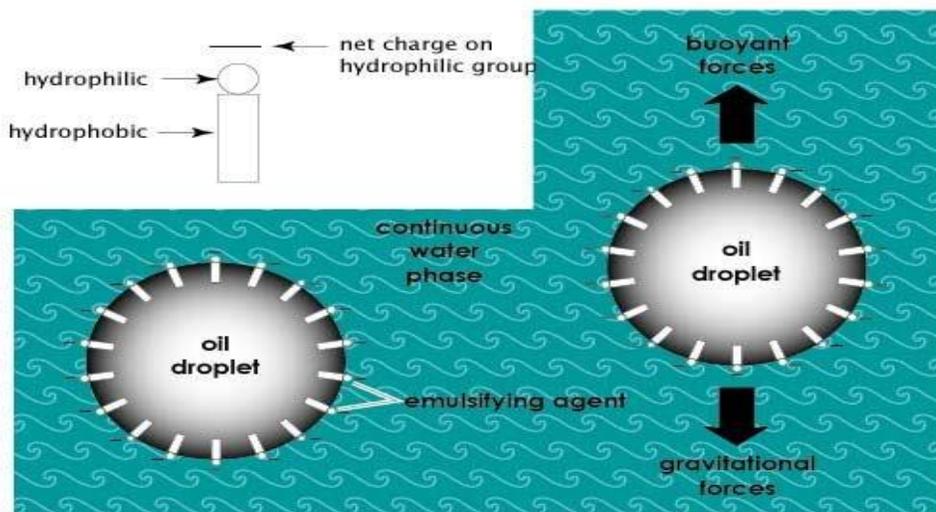
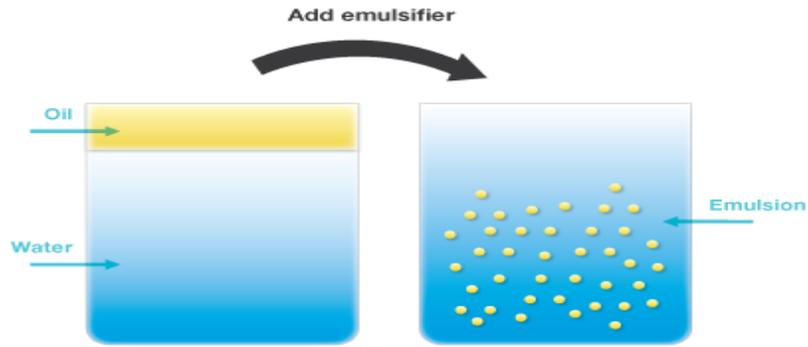


Figure 4: Schematic representation of formation of emulsion

## 2.7 Particle size measurement

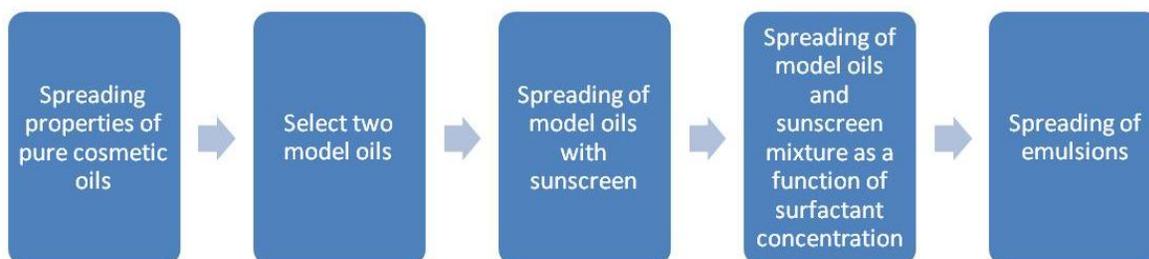
The emulsion droplet sizes were measured using laser light scattering (ex. *Malvern Mastersizer*). This instrument has a helium neon laser of wavelength of 633 nm. Light scattered by the sample is focused on to the photosensitive silicon detectors. The light falling on the detectors are measured and integrated 500 times each second. This gives a statistically significant scattering pattern of the widest distributions to be acquired within seconds and finally measures the average size of the distribution.

## 2.8 Microscopic investigation of emulsion spreading

A drop of emulsion was placed on cleaned substrates without cover slip using Hamilton micrometer syringes. The spontaneous spreading of emulsion was monitored under bright field mode, using Axioplan 2 microscope from Carl Zeiss and fluorescence images were obtained from Olympus Provis microscope. To perform measurements in fluorescence mode, the oil phase was doped with  $1.57 \times 10^{-5}$  molar solution of Nile red (ex. Sigma). This concentration of Nile red dye used does not change the properties of the oil significantly.

## 3. Results and Discussions

In this section we start the discussion, by reporting the spreading behavior of pure oils



followed by studying the spreading behavior of sunscreen with two model oils and followed by understanding the role of surfactant in spreading of oils. These studies will form the basis to understand emulsions spreading properties. We finally conclude by studying the emulsion spreading in totality. A schematic flow chart of the study is given below:

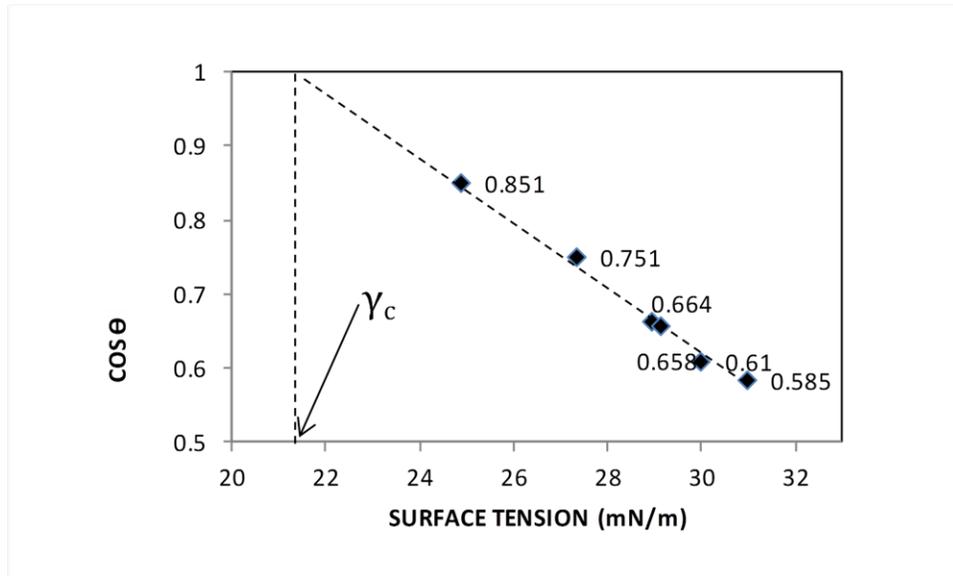
### 3.1 Spreading behavior of pure oils

Contact angle of cosmetic oils were measured on both PMMA and Teflon surface. It was observed that the cosmetic oils spread completely on PMMA surface whereas measurable contact angle was observed on Teflon surface (please refer section 2.2). Thus to amplify the inherent spreading behavior of various oils and also to obtain measurable contact angles, all further experiments were performed on Teflon surface. The surface tension of pure cosmetic oils, initial contact angle and final contact angle values on Teflon surface is presented in the *table 1*. The final contact angle

measurements were performed for 30 minutes, to ensure equilibrium. This data was used to obtain a Zisman plot to determine the critical surface tension of the Teflon substrate (*graph 1*). The Zisman plot indicated that the critical surface tension of the Teflon used is  $\sim 21$  mN/m. Thus liquids which have a surface tension lower than this value is expected to wet the Teflon surface completely. However this assumption neglects other complications such as liquid adsorbing ahead of meniscus [23]. Thus one would expect that as the surface tension values decreases the contact angle would decrease, provided the viscosity does not affect the spreading significantly. Our observation also follows the same trend except Parsol MCX and ISA. This anomaly of Parsol MCX and ISA is explained later.

<b>Cosmetic oil</b>	<b>Surface tension (mN/m)</b>	<b>Final contact angle</b>	<b>Initial contact angle</b>
MCX	$23.08 \pm 0.39$	$45.53 \pm 1.8$	$52.60 \pm 1.1$
Isohexadecane	$24.86 \pm 0.18$	$31.64 \pm 0.55$	$33.60 \pm 0.13$
IPM	$27.32 \pm 0.51$	$41.28 \pm 0.1$	$44.62 \pm 0.8$
Dicaprylyl carbonate	$28.92 \pm 0.18$	$48.43 \pm 0.87$	$52.12 \pm 1.87$
Coco-caprylate	$29.11 \pm 0.17$	$48.84 \pm 1.09$	$51.41 \pm 2.31$
Mineral Oil (LLPO)	$29.96 \pm 0.31$	$52.20 \pm 2.0$	$52.79 \pm 2.4$
Isostearyl alcohol	$30.95 \pm 0.18$	$54.23 \pm 0.92$	$56.12 \pm 0.49$
Isostearic acid (ISA)	$32.15 \pm 0.04$	$50.54 \pm 0.3$	$51.88 \pm 0.5$

*Table 1: Surface tension and contact angle of pure cosmetic oils on Teflon substrate*



Graph 1: Zisman plot of pure cosmetics oils on Teflon substrate

### 3.2 Spreading behavior of oils with sunscreen

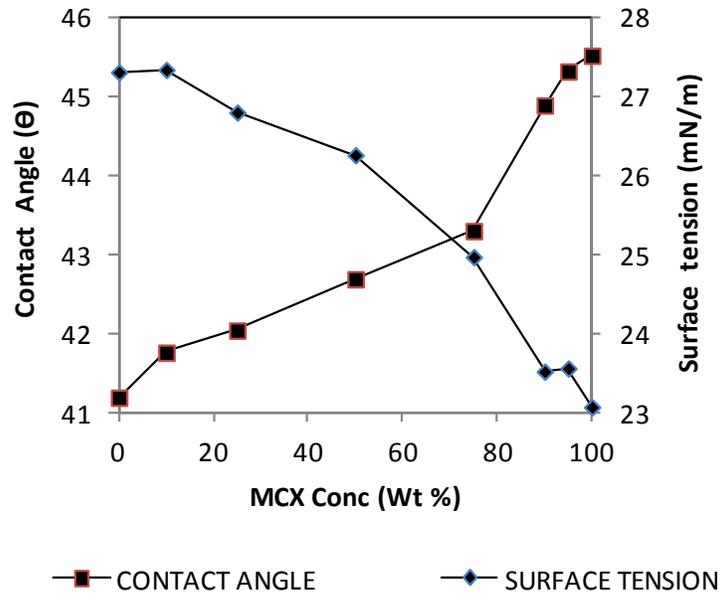
Parsol MCX is one of the widely used UVB sunscreen and is miscible with most of the cosmetic oils. In this section we present the spreading properties of this sunscreen with two model oils Isopropyl myristate (IPM) and Isostearic acid (ISA). While ISA has a higher surface tension of 32 mN/m and IPM has a relatively lower value of 27mN/m (*table 1*). Thus as explained earlier their respective spreading properties are also very different as consequence. Surface tension and contact angle values of mixture of IPM and MCX is presented in *table 2*.

Sample	Surface tension (mN/m)	Initial contact angle	Final contact angle
100% IPM	27.32 ± 0.51	44.62 ± 0.8	41.28 ± 0.1
90% IPM +10% MCX	27.35 ± 0.50	45.89 ± 2.9	41.77 ± 0.7
75% IPM + 25% MCX	26.81 ± 0.52	46.69 ± 0.4	42.05 ± 0.8
50% IPM + 50% MCX	26.27 ± 0.03	51.59 ± 2.5	42.7 ± 0.6
25% IPM + 75% MCX	24.98 ± 1.65	51.94 ± 0.3	43.31 ± 0.8
10% IPM + 90% MCX	23.53 ± 0.01	53.54 ± 0.7	44.90 ± 1.0
5% IPM + 95% MCX	23.57 ± 0.04	52.95 ± 1.0	45.33 ± 1.9
100% MCX	23.08 ± 0.39	52.60 ± 1.1	45.53 ± 1.8

*Table 2: Surface tension and contact angle of mixture of IPM and MCX*

It is observed from *table 2* that the surface tension decreases with the addition of MCX where as contact angle increases. This phenomenon is also presented in *graph 2*. This is completely contradictory to the expectation in absence of any other factors. However during the course of performing the experiments it was observed that the viscosity of these mixtures changes on addition of MCX. Hence if viscosity dominates over these equilibrium measurements, then this apparent anomaly could be explained. Thus the viscosities of these mixtures were measured and are presented along with the surface tension value in *table 3* and *graph 3*. It can be inferred from the viscosity and surface

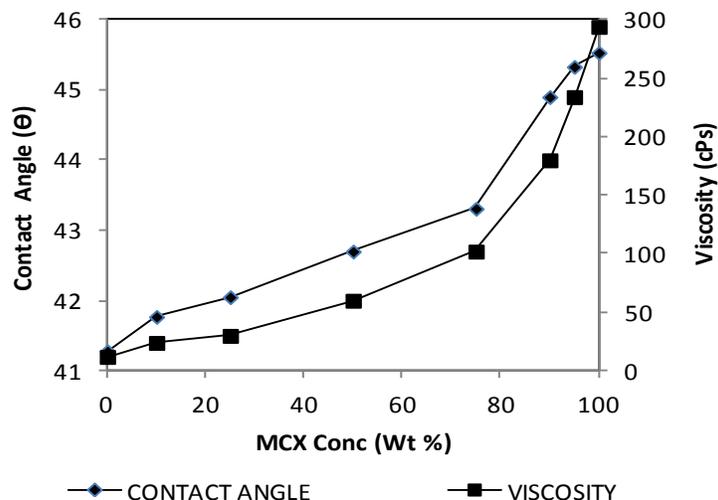
tension data that the anomaly which we mentioned earlier (section 3.1) can be explained as follows. MCX is much more viscous than the IPM; with the addition of MCX with IPM, though surface tension decreases but viscosity of the mixture increases and hence the contact angle increases.



Graph 2: Surface tension and contact angle (final) of mixture of IPM and MCX

<b>Sample</b>	<b>Surface tension (mN/m)</b>	<b>Contact angle</b>	<b>Viscosity(cPs)</b>
100% Commercial IPM	27.32	41.28	12
90% IPM + 10% MCX	27.35	41.77	24
75% IPM + 25% MCX	26.81	42.05	30
50% IPM + 50% MCX	26.27	42.7	60
25% IPM + 75% MCX	24.98	43.31	102
10% IPM + 90% MCX	23.53	44.90	180
5% IPM + 95% MCX	23.57	45.33	234
100% MCX	23.08	45.53	294

*Table 3: Surface tension, contact angle and viscosity of mixture of IPM and MCX*



*Graph 3: Viscosity and contact angle (final) of mixture of IPM and MCX*

Thus it can be inferred from the above data that not only surface tension but also the viscosity of the oil plays an important role in deciding the spreading behavior.

The contact angle and surface tension values of the other model oil, ISA and MCX are presented in *table 4*. Addition of MCX reduces both surface tension and contact angle as expected. Viscosity of ISA is 252 cPs which is not very different from MCX and hence in this case viscosity does not play a significant role unlike IPM and MCX mixture.

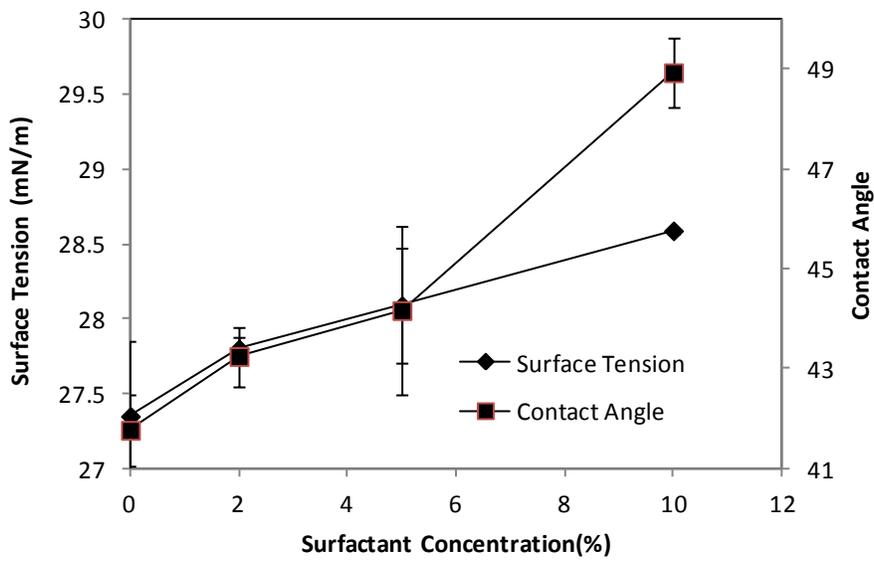
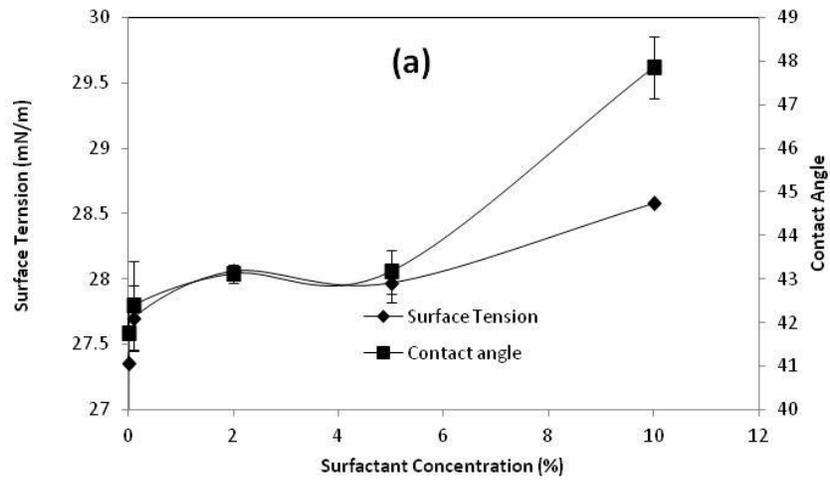
Sample	Surface tension (mN/m)	Initial contact angle	Final contact angle
100 % ISA	32.15 ± 0.04	51.88 ± 0.5	50.54 ± 0.3
90% ISA +10% MCX	31.73 ± 0.15	51.45 ± 0.0	50.28 ± 0.5
75% ISA + 25% MCX	29.39 ± 0.44	52.00 ± 0.5	48.57 ± 1.4
50% ISA + 50% MCX	28.60 ± 0.12	54.95 ± 2.4	48.37 ± 1.1
25% ISA + 75% MCX	27.65 ± 0.05	52.80 ± 1.3	47.15 ± 0.9
10% ISA + 90% MCX	23.52	55.32 ± 1.1	46.96 ± 0.7
100 % MCX	23.08 ± 0.39	52.60 ± 1.1	45.53 ± 1.8

*Table 4: Surface tension, contact angle and viscosity of mixture of ISA and MCX*

### 3.3 Spreading behavior of oils and sunscreen mixtures with surfactants

So far we have discussed the pure systems and studied their spreading behavior. In this section we introduce surfactants in the model systems and study their spreading properties. Surfactants in general are known to enhance the spreading behavior of liquid, especially aqueous liquids. In order to understand the effect of surfactant on spreading behavior of oils, we have tested two nonionic surfactants: C<sub>12</sub>EO<sub>3</sub> and C<sub>12</sub>EO<sub>7</sub> at various concentrations with the two model oils ISA and IPM. The spreading properties of these model oils were presented earlier of their respective pure system

and in conjunction with the sunscreen MCX. It was observed that incorporation of these nonionic surfactants to IPM–MCX mixture does not result in significant contact angle and surface tension (*graph 4*). The data presented below is for a concentration of 90% IPM and 10% MCX with various surfactant concentrations. In absence of surfactants, the mixture has a surface tension value of ~27mN/m which does not change significantly upon addition of surfactants. This is probably due to the fact the concentration of surfactants used is already above the saturation limit to cause further change in its surface tension properties. Moreover in both cases the contact angle shows a slight increase. This could be due to the higher viscosity of surfactant over the oils and surfactant *per se* forms higher contact angle than oils. The mixture of ISA and MCX with surfactants also follows similar trends and hence not presented here. Apart from this, we also tried to see the effect of these non-ionic surfactants on pure two model oils. In these measurements no significant change was observed either in surface tension or in contact angle values (*Appendix2*).



Graph 4: Surface tension and contact angle of IPM-MCX mixture with (a)  $C_{12}EO_7$  and (b)  $C_{12}EO_3$  at various concentrations

### 3.4 Spontaneous Spreading behavior of emulsions

In the previous section we have discussed on the spreading properties of pure oils and oils along with sunscreen and surfactant as a function of concentration. In this section we discuss the effect of introducing the continuous phase i.e. water and relate the behavior with the pure systems. Interfacial tension of oils plays a critical role in dictating the emulsion properties and hence the droplet size of the emulsion. Model oil should ideally represent most of the cosmetic oils in term of their properties and the droplet size of the emulsions should be in the measureable domain of microscopy. The IFT values of common cosmetic oils are presented in *table 5*. It is observed form the table that oil like IPM has a value which is almost in the median range and is well suited for the emulsion studies. In other words the model oil should not have either extremely low or high interfacial tension with water. On the other hand pure hydrocarbon oils (e.g. LLPO) has higher IFT due to the weaker interaction (by van der waals force) of hydrocarbon chain. Isohexadecane exhibits lowest surface tension value compared to the rest of the liquid but its IFT value is still higher. As the interaction starts moving from pure van der waals to polar interactions, IFT value decreases further. This can be clearly seen from the IFT value of IPM and coco-caprylate. We have measured the lower IFT values for Isosteryl alcohol and ISA and in both these cases the observed IFT value could be not only be due to the polar interaction but also due to the hydrogen bonding interaction of alcohol and acid group respectively. So, it can be seen that higher the level of the interaction of oil with water, lower will be the IFT values. Interfacial tension value of MCX could not be measured by Wilhelmy plate method due to higher density of MCX than water and MCX wets the surface of the water immediately (*Appendix3*). Thus considering these facts, IPM was used as model oil for emulsion studies for future experiments.

Liquids	IFT (mN/m)	Surface Tension (mN/m)
Isohexadecane	31.45 ± 3.09	24.86 ± 0.18
IPM	27.45 ± 0.67	27.32 ± 0.51
Coco-Caprylate	21.94 ± 1.05	29.11 ± 0.17
Mineral Oil (LLPO)	45.65 ± 0.57	29.96 ± 0.31
Isostearic Alcohol	14.1 ± 0.16	30.95 ± 0.18
ISA	15.55 ± 0.06	32.15 ± 0.04

*Table 5: Interfacial tension of oils with water and surface tension of pure oils*

Another critical factor determining the nature of emulsions is the nature of emulsifier used. Typically the emulsifier used for emulsions are classified by their HLB number. We have tried making emulsions with relatively higher HLB surfactant i.e. C<sub>12</sub>EO<sub>7</sub> whose HLB value is 12.9. The concentration of the surfactant to be used for the studies was decided after performing IFT and droplet size measurements as discussed before. It was observed that the IFT value saturates after a concentration of 2 % and but the droplet size of the same is also relatively smaller to be measureable under optical microscopy. A concentration vs droplet scan suggests that 0.5 % surfactant has the optimum droplet size to be measured by optical microscope and its IFT is also not much different from the saturation value. The IFT value and the droplet size are presented in *table 6* and *7*.

Cosmetic Oil	0.5% C <sub>12</sub> EO <sub>7</sub> (mN/m)	1% C <sub>12</sub> EO <sub>7</sub> (mN/m)	2% C <sub>12</sub> EO <sub>7</sub> (mN/m)
IPM	1.5 ± 0.2	0.77 ± 0.09	0.58 ± 0.07

Table 6: Interfacial tension of IPM water system with various concentration of surfactant

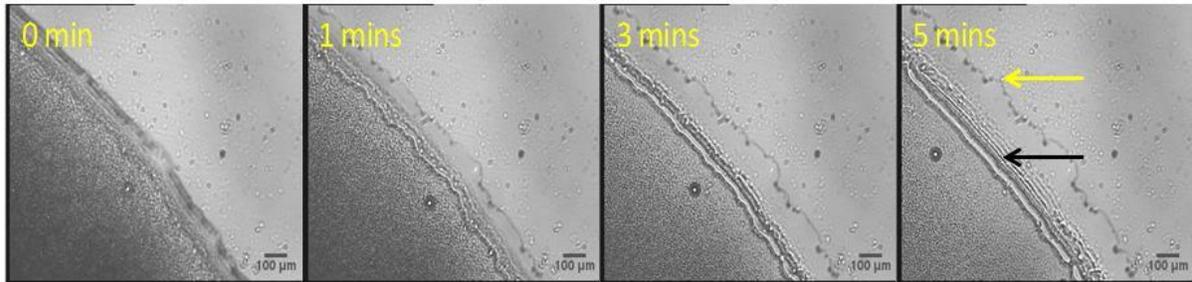
Liquid	Time	D(0.1) µm	D(0.5) µm	D(0.9) µm
IPM	Initial	2.2	4.06	7.4
	30 mins	2.2	4.06	7.4
	120 mins	2.2	4.08	7.5

Table 7: Particle size of IPM emulsion with 0.5% concentration of C<sub>12</sub>EO<sub>7</sub>

Emulsion containing 10 % IPM and 0.5 % C<sub>12</sub>EO<sub>7</sub> was used for the spreading studies. Two substrates were used for these measurements. A standard glass slides which serves as a model high energy surface and Teflon a model hydrophobic surface were used. The spreading behavior difference between these two substrates will help us to explain the phenomena under two extreme conditions.

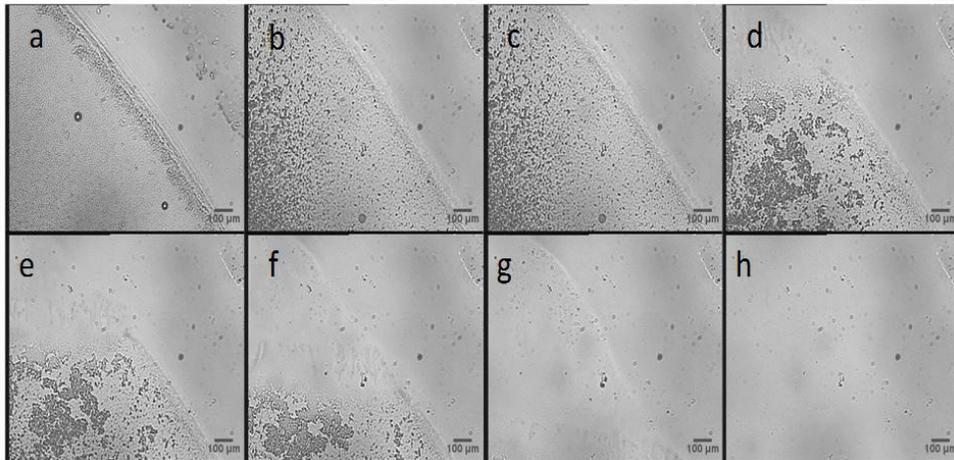
The droplet of emulsion was kept on the surface of glass and was monitored over a period of time. The figure shows the bright field images of the emulsion drop spreading over a period of time. Yellow line indicates the precursor film's front and black line indicates rim of accumulation of emulsion droplets (pinning of droplets). Over a period of time, precursor films moves ahead whereas the rim of droplets is not and it seems like

precursor film does not carry any emulsion. After certain duration, precursor film movement stops.



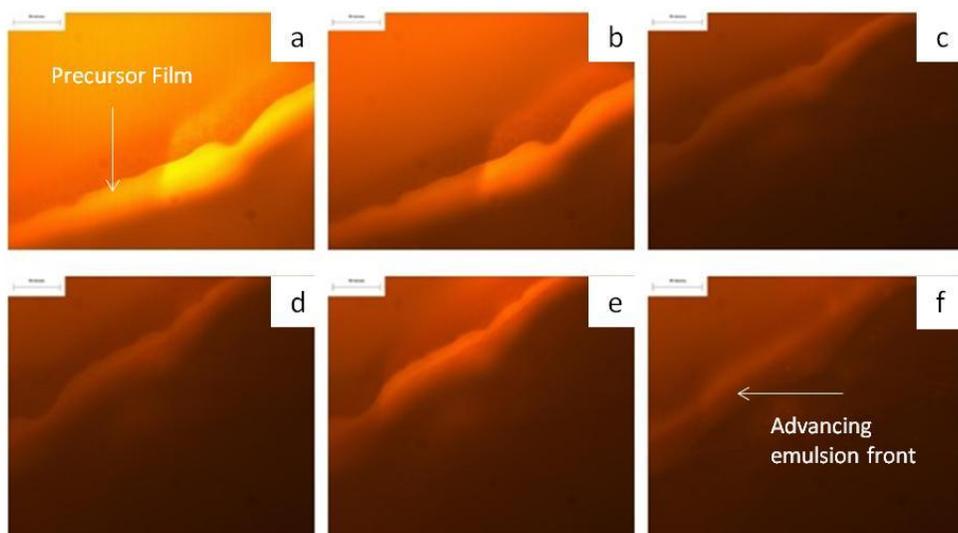
*Figure 5: Movement of the meniscus of an emulsion droplet on glass substrate*

The spreading of emulsion droplet between 10<sup>th</sup> and 11<sup>th</sup> minutes is presented in figure 6. It can be inferred from the series of images that emulsion drop breaks (coalesce) as water evaporates. Once the droplets are broken, the coalesced oil spreads completely. Whether the coalesced oil spreads on top of the water or on the substrate need further investigation.



*Figure 6: Spreading of emulsion droplet on glass surface between 10<sup>th</sup> and 11<sup>th</sup> minute*

Similar experiments were performed on Teflon surface. The phenomena were monitored through fluorescence microscopy (*figure 7*). It was observed that the droplet spreading is slower compared with the glass substrate. Precursor film moves shorter distance in Teflon than in glass and precursor film is probably the water continuous phase with dissolved surfactants and need further techniques like Ellipsometry and AFM to establish the exact mechanism of spreading on surfaces.



*Figure 7: Spreading of emulsion droplet on Teflon surface*

## 4. Conclusion

In this work, we have studied the spreading behavior of cosmetic oils along with sunscreen on two hydrophobic substrates i.e. PMMA and Teflon. It was observed that most of the cosmetic oils used, spread completely on PMMA where as on Teflon it makes certain contact angle. Based on the spreading experiments, we found through Zisman plot that critical surface tension of Teflon is  $\sim 21$  mN/m. We found anomaly in spreading, in case of mixture of IPM and MCX and based on our finding, we concluded that not only surface tension but also viscosity of oil plays important role in spreading phenomenon. We also measured the IFT of pure oils with and without nonionic surfactant and in case of pure oils, lower IFT value is observed when the interaction happens through hydrogen bond interaction and higher IFT values are obtained when the interactions are van der waals in nature. A nonionic surfactant of relatively higher HLB  $C_{12}EO_7$  was used for emulsion studies whose IFT value with IPM-Water system attains the value of  $\sim 0.5$  mN/m at 2 % surfactant level and we also measured the emulsion droplet size with various concentration of surfactant. It was observed that smaller droplet sizes were obtained at higher surfactant concentration. Spontaneous spreading of IPM emulsion with  $C_{12}EO_7$  as surfactant on glass and Teflon was performed. It was observed that in case of glass, precursor film first moves where as emulsion droplets are not spreading further and they are pinned. After a period of time, emulsion droplet coalesces and spreads completely. In case of Teflon, we found that movement of precursor film was very slow and the distance travelled by the film was less compared to glass. These observations of spreading on these two substrates needs to be further validated through Ellipsometry and AFM techniques.

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## APPENDIX 1

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**The trade name and INCI (*International Nomenclature of Cosmetic Ingredients*) name of pure cosmetic oils:**

<b>TRADE NAME</b>	<b>INCI NAME</b>
MCX	Ethylhexyl Methoxy Cinnamate
Arlamol HD	Isohexadecane
IPM (Isopropyl Myristate)	Tetradecanoic Acid, 1-methylethyl ester
Ceitol CC	Dicaprylyl Carbonate
Ceitol C5	Coco- Caprylate
LLPO	Mineral oil
Prisorine 3505	Isostearic acid
Prisorine 3515	Isostearic alcohol

*Table: Trade name and INCI name of pure liquids*

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## APPENDIX 2

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### Spreading behavior of oils with surfactants

The following tables contain the effect of surfactants on individual oils and on oils and sunscreen mixtures which didn't show any considerable change

SAMPLE	FINAL CONTACT ANGLE	INITIAL CONTACT ANGLE
Commercial IPM	41.28	44.62
2% C <sub>12</sub> EO <sub>7</sub> + 98% IPM	42.4	43.9
10% C <sub>12</sub> EO <sub>7</sub> + 90% IPM	42.2	45.7

*Table: Effect of C<sub>12</sub>EO<sub>7</sub> concentration on IPM*

Sample	Final Contact Angle	Initial Contact Angle
2% C <sub>12</sub> EO <sub>3</sub> + 98% IPM	39.80 ± 0.79	43.75 ± 0.07
10% C <sub>12</sub> EO <sub>3</sub> + 90% IPM	40.28 ± 1.27	46.66 ± 0.60

*Table: Effect of C<sub>12</sub>EO<sub>3</sub> concentration on IPM*

Sample	Surface Tension	Final Contact Angle	Initial Contact Angle
2% C <sub>12</sub> EO <sub>3</sub> + 98% Prisorine 3505	30.63 ± 0.53	52.22 ± 0.1	53.9 ± 0.38
5% C <sub>12</sub> EO <sub>3</sub> + 95% Prisorine 3505	31.37 ± 0.14	54.21 ± 0.25	54.89 ± 0.60
10% C <sub>12</sub> EO <sub>3</sub> + 90% Prisorine 3505	31.27 ± 0.06	53.72 ± 2.6	55.03 ± 1.68

*Table: Effect of C<sub>12</sub>EO<sub>3</sub> concentration on ISA*

## APPENDIX 3

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### Reason for not measuring the IFT of MCX:

Except MCX, all liquids are less dense than water (table). Therefore in this case, MCX cannot act as a light phase with water. When we tried to cover water with MCX to form an interface during IFT measurement, both the liquids tried to settle down at the bottom due to which we didn't get proper horizontal interface for its measurement. The density of the pure oils is given below:

<b>PURE LIQUIDS</b>	<b>DENSITY (g/cm<sup>3</sup>)</b>
Water	1.0
MCX	1.01
Arlamol HD	0.79
Commercial IPM	0.85
Ceitol CC	0.89
Ceitol C5	0.86
Mineral Oil (LLPO)	0.83
Prisorine 3515	0.88
Prisorine 3505	0.88

*Table: Density of pure liquids including water*

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### Use of Image J software for measuring contact angle

Image J software is designed for easier and more accurate measurement of contact angle. But this software does not support .bmp format which is obtained from the Kruss Goniometer, therefore we need to convert it to .JPEG format before proceeding further. Once the image is ready, we can drag it to the Image J window and convert it to *Grayscale* by going to Image→ Type→ 16-bit. Then we need to click *Plugins*→ *drop analysis*→ *Dropsnake* and then manually plot points on the edge of the liquid drop and double-click it. Just after double-clicking, the left hand side angle and the right hand side angle will be displayed on the top left corner of the screen as shown in fig 2.1. The required contact angle will be the average of these two angles. There is another plug-in called Low Bond Axisymmetric Drop Shape Analysis (LBADSA) which is accurate up to two decimal points but that plug-in requires a shadow of the drop on the substrate which was missing in our images due to opaqueness of the substrate. Hence we used *Dropsnake* plugin.

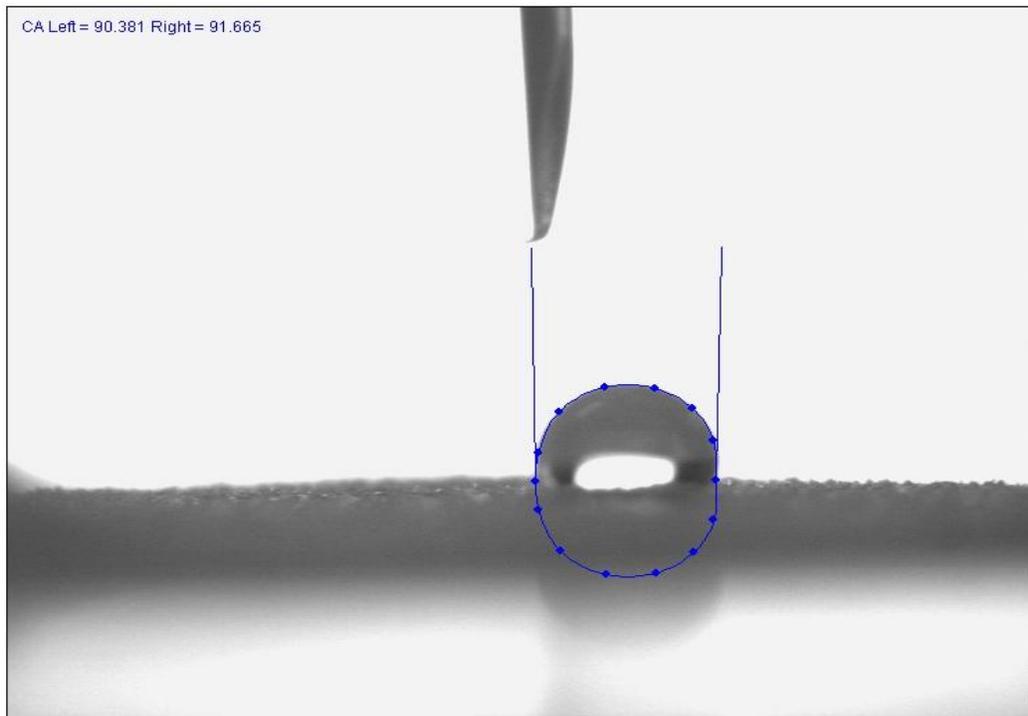


Fig: Water droplet on vitro skin

