

Importance of Interfacial Rheology and its Applications

Review of the Interfacial Rheology

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Abstract : It is important to study the interfaces in case of fluid mechanics as they play a very important role for the separation of two fluids. The properties of these materials can be manipulated and controlled as per the need, but before this, we have to optimize these properties for knowing the peak points. Also for the deformation of any fluid, we have to know their viscoelastic properties. The following research is made on the subject of Interfacial Rheology to understand the basics of this subject. In this study, we would understand what the Interfacial Rheology is and what are its various applications in different instruments. For this, we have to recall the concepts like interface, surface tension and interfacial tension, Rheology, surfactants etc. After knowing what the Interfacial Rheology is and what are its applications, we discuss in details of different types of Rheometer like Spinning drop Tension meter, Langmuir Blodgett trough, Interfacial Shear Rheometer, Bi-cone geometry Rheometer etc. While studying these instruments we focus on its working principle, handling, selectivity and conclusions. The future scope of this research is also mentioned to encourage the new research in field of interfacial science and Rheology.

IndexTerms - Interface, Rheology, Surface tension, Rheometer.

1. INTRODUCTION

The study of deformation of any flow is referred as Rheology. In other words, it is the study of response of material to applied forces or deformations. Interface is a separating region between two fluids. The properties at the interface are different from the two phases it separates. These interfaces are non-stationary and can be deformed by applying force. A large number of materials in food, pharmaceutical, and petroleum industries are in the form of foams or emulsions and it is very important to know the interfacial properties to stabilize or destabilize them. Interfacial properties play a major role in understanding and preventing film drainage of foams or coalescence of emulsions. The complexity of interface arises because of the presence of Amphiphiles molecules on the interface for example proteins in food products, Fat globules in ice cream, asphaltene in crude oil etc [1, 2, and 3]. We often tend to use the continuity of stresses boundary condition at the interface existing between the phases and that is not valid if we have a complex interface [4]. All these things make it challenging theoretically because of the complexity of boundary conditions the interface and experimentally because shear and dilatational properties are not readily accessible. The processes occurring at the interface can significantly influence the overall behavior of the system if it has a sufficiently large interfacial area. In cases of foam and emulsions, the motion of interface will considerably influence the bulk motion and coupling of interfacial flow with the shear flow will be significant. For characterizing an interface, we need to find its thermodynamic properties, its microstructure and for its rheological properties, we need to find how it responds to deformation. There are two ways to deform an interface one at the constant area and changing shape (shear) and other at changing area while maintaining the shape (dilatational). Study of the interface is important in many technical applications for example emulsification, high-speed coating, foaming etc. Surface rheology treats a discontinuous system in terms of continuum theory. For rheologists and engineers, the problem is to find how the flow of a liquid is affected by the presence of a mobile interface. A fluid interface affects liquid motion because the stress tensor in the interface differs from that in the adjoining bulk fluids, as a result of the contribution of the surface tension. In solving the hydrodynamic equations of liquid motion, the interfacial stress-tensor components must appear in the boundary conditions at the free surface. The magnitude of the interfacial stress-tensor components depends on the interfacial composition, and on the liquid motion at and near the surface. The relation between deformations and corresponding tractions in the

surface can be described in terms of the formalism developed in 3-D rheology. The parameters occurring in this relation define the viscous and elastic properties of the surface.

The present study reviews some recent work in which the subject is approached from a phenomenological point of view. The surface rheological parameters are introduced by means of operational definitions. Measured values of these parameters may subsequently be interpreted in terms of other measurable quantities. Several other approaches to the subject of surface rheology are possible. One starts with a molecular picture and attempts to describe the behavior of a system containing a fluid interface in terms of molecular properties. This is a very ambitious goal, considering that the apparently simpler properties of liquids, such as Newtonian viscosity and equilibrium surface tension, cannot yet be explained in terms of a molecular model. This kind of approach to the subject of surface rheology has been reviewed recently [5]. Another possible approach follows Boussinesq [6] in postulating that the interface itself behaves as a 2-dimensional body, to which concepts and results derived from the usual 3-D rheology can by means of simple analogy be applied. This approach has led, on the one hand, to a preoccupation with purely viscous properties of the surface [7-11], and on the other to a search for “intrinsic” surface properties, i.e. properties that can be attributed to an isolated, autonomous 2-dimensional phase [12]. One of the most important properties of a fluid interface, however, is that it cannot be autonomous: it exists only as a boundary of a bulk fluid. Any deformation or motion of the surface causes some corresponding motion of the adjoining bulk fluids. In most cases, and certainly in all those of practical interest, the motion will also change the local composition and the stress tensor, both at the surface and in the adjoining bulk fluids. All attempts to identify “intrinsic” surface properties implicitly assume that the observed effects can be divided into those attributable to the surface and those due to phenomena occurring within the bulk of the liquid. Such a separation is, however, only possible for a system in thermodynamic equilibrium, by the introduction of excess quantities and a dividing surface to which these quantities must be assigned [13]. In a rheological experiment the equilibrium is necessarily disturbed, and then there is no general and unambiguous way of separating bulk and surface contributions. The distinction between the two is, therefore, somewhat arbitrary, and one may expect that the result will depend on the method used.

One important consequence of the non-autonomy of a fluid interface is the existence of a type of deformation that cannot be realized in a bulk material. A new surface can easily be made to appear somewhere, an older one to disappear somewhere else. There is no 3-D analogue: even in a measurement of volume viscosity or bulk modulus the amount of material is constant. It is evident that a 2-dimensional analogue of the continuity equation cannot be valid for the surface alone. It follows that two different types of deformation must be considered in the surface: one in which the area of every surface element remains unchanged and only the resistance to a change of shape is measured, and another in which the shape is constant but the area is varied. The latter type of deformation is characteristic of surface rheology because it involves creation and annihilation of the surface. It is also the more important deformation in most practical applications [12]. In a much-neglected paper [14] it is demonstrated that “what a water surface resists is not shearing but local expansion and contraction of area, even under conditions that the total area shall remain unchanged” The behaviour of a surface when both area and shape are varied has been discussed [9,10] only on the basis of simplifying approximations, involving purely viscous (Newtonian) behaviour with viscosity coefficients independent of the local surface composition. As we shall see, the non-linear viscoelastic surface behaviour is the rule rather than the exception. For our purpose, it is sufficient to consider only deformations in the plane of the surface. The formalism required to include deformation of the surface itself has been developed in great detail [10], but it will not be needed in a discussion of the measurement and the physical interpretation of surface rheological parameters.

Emulsions are encountered in our day to day life and it is important for food products such as butter, milk, margarine, ice creams. But this phenomenon causes a severe problem in the petroleum industry. The crude extracted from reservoirs is passed through pumps, reservoirs and various units in which it is agitated vigorously and a stable emulsion of oil water is formed and it is very difficult to separate [15,16]. The problem in separating this emulsion is because the mechanism of stabilization of this oil-water emulsion is not fully understood. The salts present in the water can cause severe corrosion problem [17]. Because of the

formation of stable crude oil-water emulsion problems like catalyst deactivation, corrosion, transportation arise which ultimately results in increased cost of production [18, 20]. Knowledge of the rheological properties for petroleum oil is very important for its migration within the reservoir or from the oil well to petroleum refining unit [21]. There is a lack in the available rheological properties especially for heavy crude oil because of the complexity of components present [3]. The viscosity of the heavy crude oil is generally in the range of $1e3$ to $1e5$ mPa.s, with API gravity of lower value around or less than 20 [2].

A major constituent of heavy crude oil is asphaltenes and resins. It contains fewer amounts of light hydrocarbons [1, 16]. Because of complexity in the components present in crude oil rheological properties are not readily available [3]. Asphaltenes are insoluble in lighter paraffin like n-pentane or n-heptane but they get solubilised in light aromatic solvents like toluene and benzene. Asphaltenes, resins, small solids and waxes are the major constituents of oil and they migrate to form highly viscous or rigid films at the oil-water interface, they build a barrier for coalescence of droplets which further results in a stabilized oil-water emulsion. It is essential to remove water to get adequate export oil quality and to avoid corrosion problems.

2. Measurement Fundamentals for Interfacial Properties

2.1 Wilhelmy Plate Method:

Wilhelmy Plate method is used to measure Static Surface Tension. A vertically suspended plate touches a liquid surface or interface, then a force F correlates with the surface tension or interfacial tension γ and with the contact angle θ according to the following equation,

$$\gamma = \frac{F}{L \cos \theta}$$

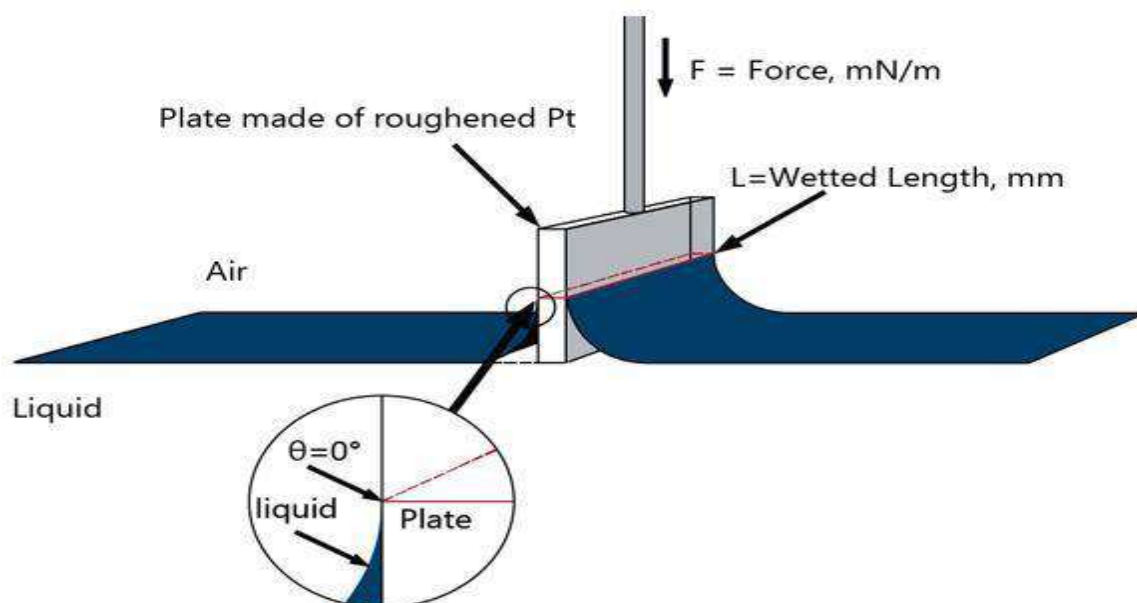


Figure 2.1: Schematic Diagram of Wilhelmy Plate Method

The plate is oriented perpendicularly to the interface and the force exerted on it is measured. The plate is moved towards the surface until the meniscus connects with it. The force acting on the plate due to its wetting is measured by a microbalance. To determine the surface tension γ the Wilhelmy equation is applied. If the plate has a wetted parameter 'd' and its weight is W_{plate} , then the force F needed to detach it from the liquid surface equals:

$$F = W_{\text{plate}} + 2 d \gamma \cos \theta \quad d = L + t$$

Where, t is thickness of plate and l = length of plate as shown in figure.

Multiplying by 2 to above equation is needed because the surface tension acts on both sides of the plate. If the liquid wets completely the plate, then $\cos\theta = 1$ and the surface tension is expressed by,

$$\gamma = (F - W_{\text{plate}}) / 2 * d * \cos\theta$$

Platinum is chosen as the plate material when measuring the SFT (surface tension) or IFT (interfacial tension) as it is chemically inert and easy to clean, and because it can be optimally wetted on account of its very high surface free energy and therefore generally forms a contact angle θ of 0° ($\cos\theta = 1$) with liquids.

2.2. Langmuir Blodgett (LB) Trough Method:

There are two types of complex interfaces one with soluble materials known as Gibbs monolayer and other with insoluble monolayer referred as Langmuir film. In the case of Gibbs monolayer, there is an equilibrium established and a relationship exists between the concentration of molecules in the water and at the interface. In the case of Langmuir film, these insoluble molecules reside only on the interface and one technique for preparing such films is LB technique.

In this, we vary the surface area and measure the surface tension and hence surface pressure with the help of Wilhelmy plate. This device can be used to establish the thermodynamic state of the insoluble material.

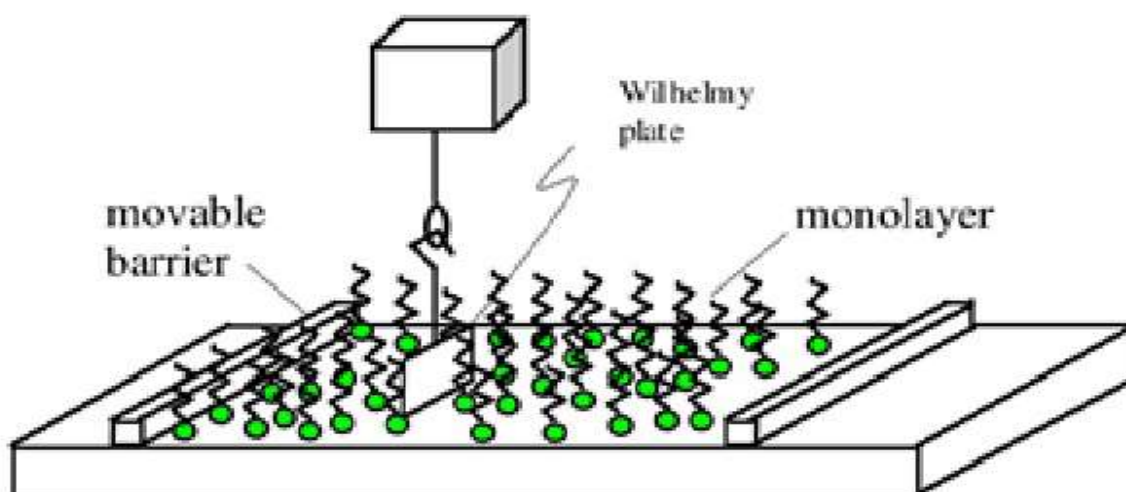


Figure 2.2: Schematic of Langmuir trough

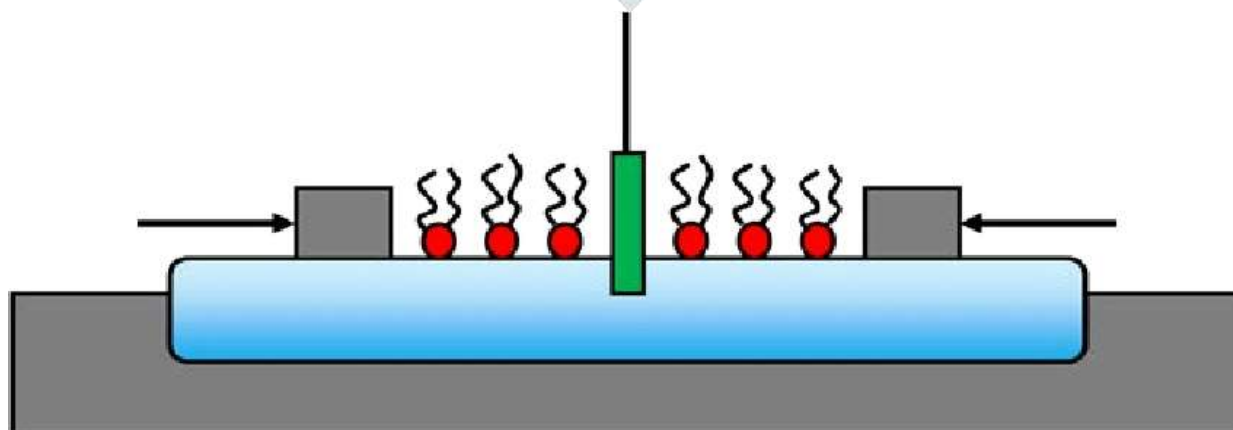


Figure 2.3: Schematic of Langmuir monolayer

2.3. Drop shape Tensiometer (DST):

In this change in shape of the drop is measured as a function of time. It is applied to the large droplets deformed by gravity. By applying balance between the forces acting on the drop (gravitational and interfacial tension) interfacial tension of the drop can be measured. By data fitting using Young Laplace equation interfacial tension can be measured.

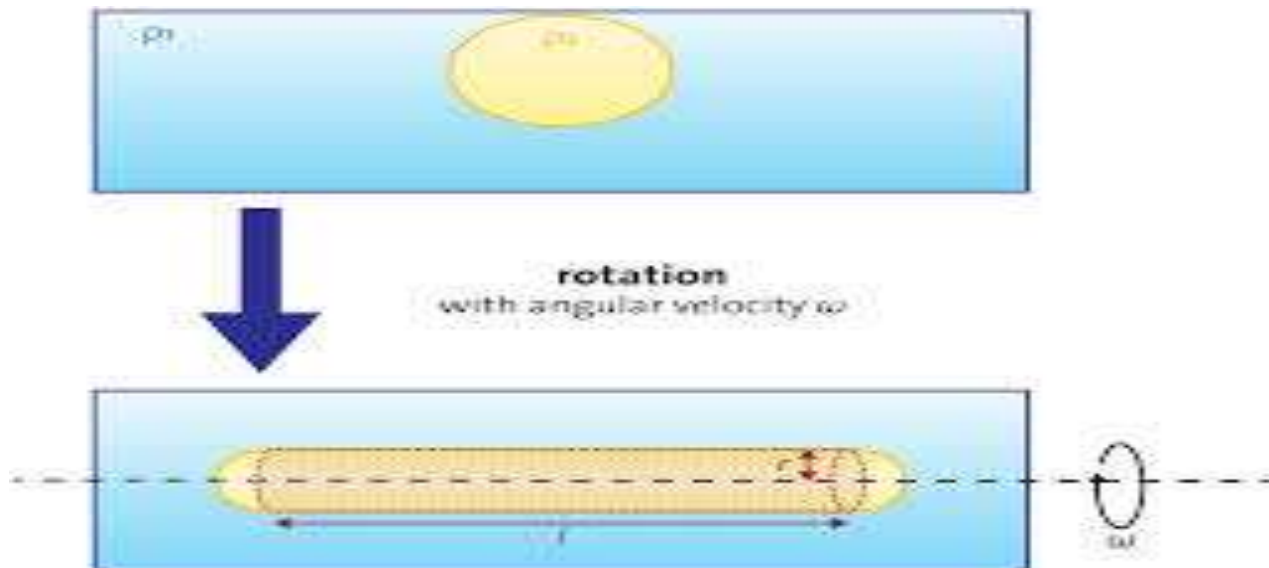


Figure 2.4: Schematic Drop shape Tensiometer

2.4. Capillary pressure Tensiometer (CPT):

It is based on the Young Laplace equation and it is used for pure liquid. In this capillary pressure inside the droplet is measured to find interfacial tension. It has an advantage that smaller droplets can be used as compared to DST. Various techniques are available to determine dilatational rheology and almost all of them are based on drops. In almost all of them, the analysis is carried out on drop/bubble shape, pressure or volume to determine surface tension.

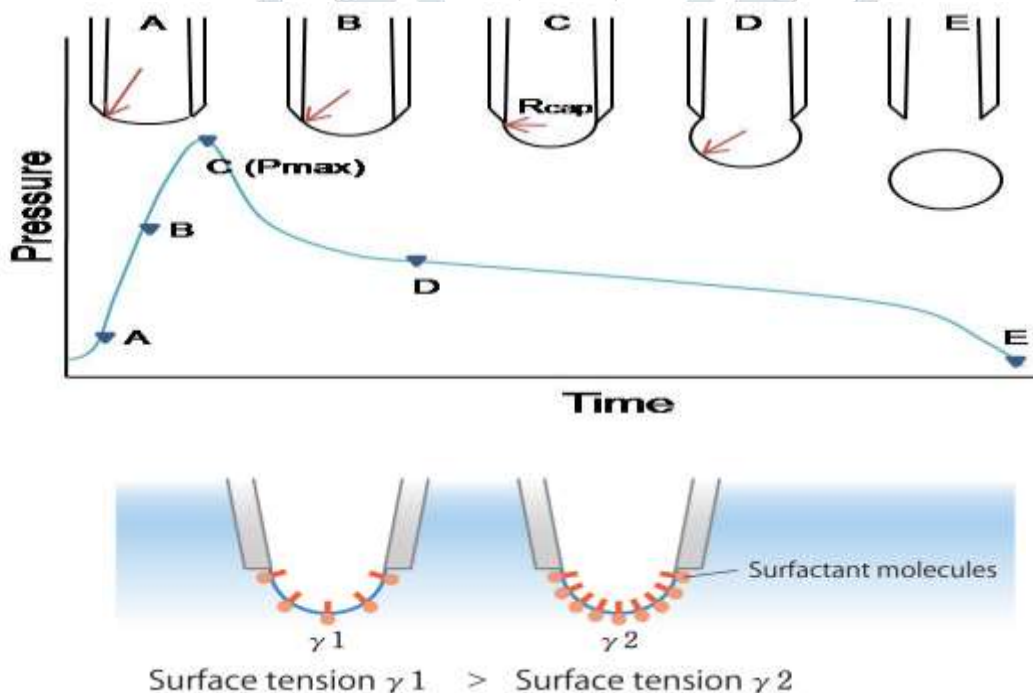


Figure 2.5: Schematic of Capillary pressure Tensiometer

3. Testing Methodologies for Interfacial Rheology

The methods used for measurement of interfacial shear rheology can be categorized into indirect and direct methods. In the indirect method, inert visible particles are used to measure the velocity profiles by image analysis and then shear interfacial characteristics can be evaluated. The indirect method the torque or displacement of a probe located in the interface is measured directly. Usually, interfacial layers are weak and high-resolution sensors for torque and displacement are required for this purpose. The source of error in these measurements may be because of Marangoni stresses or young Laplace pressure. When we deform the interface we unavoidably deform the bulk phases and measurement given is the superposition of both due to bulk and surface stress. To capture a region where interfacial stress response dominates Boussinesq no. is defined as,

$$B_0 = \frac{\mu_s}{\mu R}$$

R is the typical length scale of measuring probe related to the ratio of the area over which the bulk stresses of the measuring probe acts to the perimeter in contact with the interface. We always want Boussinesq number high to so that there is not a considerable superposition of bulk properties to the surface properties. To ensure a good design of interfacial measurement geometry R is minimized.

Most of the rheometer consists of a stationary dish and a rigid coupling between an oscillatory or rotating measuring probe and the motor that can detect displacement and torque. According to the geometry of probe different surface Rheometer such as knife-edge Rheometer, Disk surface Rheometer, Blunt knife Rheometer, Double wall ring Rheometer, Bi-cone Rheometer, Magnetic Needle Rheometer are used.

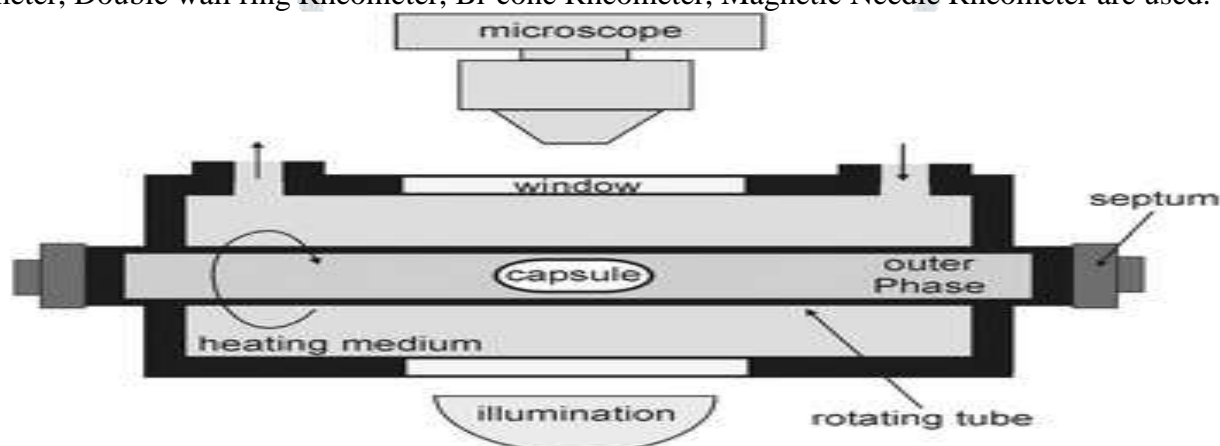


Figure 3.1: Spinning Drop Tensiometer

Magnetic needle geometry is considered a very good design from this point of view. These geometries can be used with a Rheometer for performing a large number of rheological tests including rotational or steady flow curve measurements, oscillatory or dynamic testing. Moreover, stress relaxation, creep and creep recovery, the startup of steady shear, etc. can be performed.

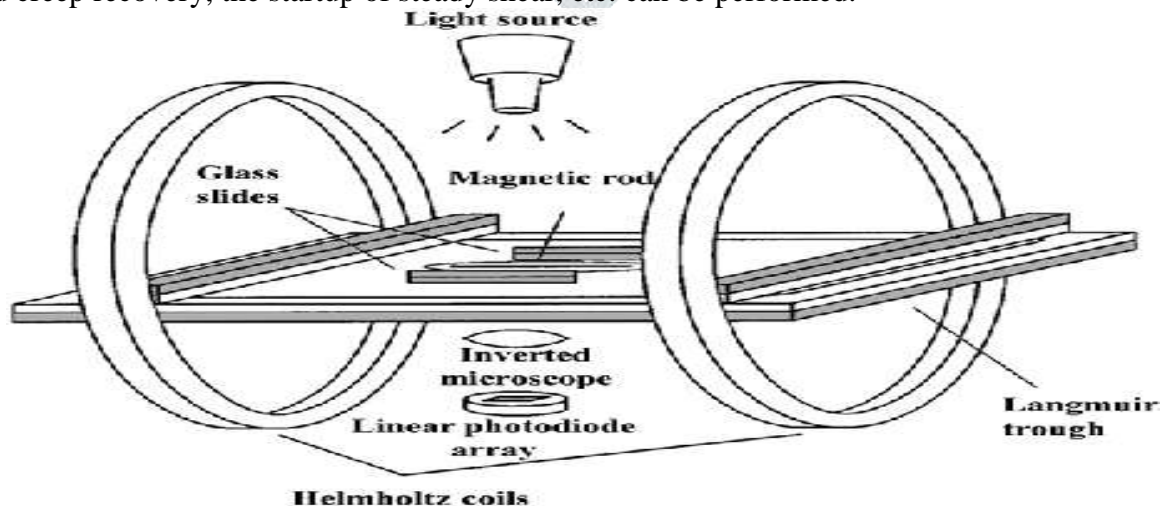


Figure 3.2: Magnetic Rod Interfacial Rheometer

Bi-cone geometry is very robust and sometimes sharp edges may result in pinning of the interface. Also, it has substantial inertia, limiting the sensitivity at high frequency or the use in transient rheological measurement. The characteristic length scale R also reduces its sensitivity as it has comparatively higher Boussinesq number as compared to needle geometry. The advantage of Magnetic rod Rheometer is that it can be easily combined with Langmuir trough which provides good control of the thermodynamic state. Hence the data can be obtained at varying pressure and temperature of the interfacial monolayer. R is very less in case of needle geometry which increases Bo number for given viscosity ratio

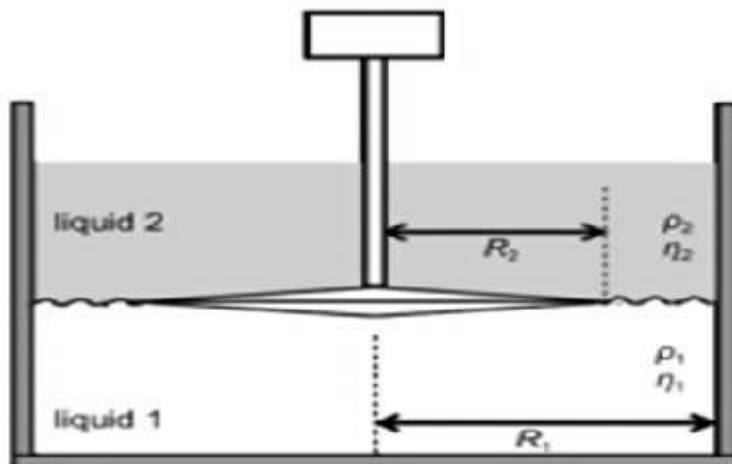


Figure 3.3: Bi-cone geometry Interfacial shear Rheometer

3.1 Interfacial Dilatational Rheology:

Interfacial Dilatational rheology describes the response of interface with compressions and expansions. Dilatational deformation changes in the area while maintaining the shape unchanged. It is important in many processing operations such as foam production, fiber spinning, blow molding, thermoforming etc. The interfacial dilatational modulus (E) is the ratio of variation in interfacial tension (γ) per unit variation in the relative surface area (A)

$$E = \frac{d\gamma}{d(\ln(A/A_0))}$$

E is a complex function when viscoelastic interface exhibits viscoelastic behavior.

$$E = E' + iE''$$

$$E = \omega * \eta_d$$

η_d is dilatational viscosity

Instruments which are most commonly used for measurement of interfacial dilatational rheology are spinning drop Tensiometer and pendant drop Tensiometer. Spinning drop Tensiometer can be used for the measurement of low interfacial tension normally below 1mN/m. This range shows that this can be used when we have surfactants present at the interface. In this, the effect of the gravitational field is neglected. This consists of a capillary filled with a low-density drop within the denser phase. When the centrifugal force is applied on the tube the deformation of drop takes place and shape of the drop changes. The interfacial tension is a function of the speed of rotation, the density of both the phases and shape of the deformed drop. By varying rotational speed periodically, the phase lag between the change in area and rotational speed can be measured and hence viscoelastic properties of the interface can be obtained. The advantages of this instrument, the contact angle are not required in this and there is no need to estimate the curvature at the interface. This method can't be used in case of liquids that have high interfacial tension. The pendant drop is a drop which is suspended from a needle in a bulk gaseous or liquid phase. The shape of the drop results from the relationship between the surface tension or interfacial tension and gravity. In the pendant drop method, the surface tension or interfacial tension is calculated from the shadow image of a

pendant drop using drop shape analysis. The dynamic pendant drop method looks at the change of the cross section of a drop emerging from a nozzle. Surface tension measurements at very short time intervals can be performed in order to monitor the change of the surface tension with time.

4. Conclusion and Future Scope of Research

The most important results from the point of view of fluid dynamics are:

1. The surface of a Newtonian liquid exhibits, in general, viscoelastic properties in extension and compression, but not necessarily in shear.
2. Methods of measuring these properties are available.
3. Coupling of liquid flow and surface behavior occurs by means of the tangential stress boundary condition.

Main applications of rheological study can be found in oil industries where asphaltenes and different types of oil are to be separated from crude. Water present in crude oil creates several problems and increases the cost of oil production. Some forms of the oil-water emulsion are extremely difficult to separate. The density difference between water and oil can cause some separation by natural coalescence and gravity settling but small fractions of dispersed water droplets will probably remain there which are very difficult to separate due to low settling velocity. As mentioned earlier asphaltenes facilitate the formation of a stable oil-water emulsion and make its separation difficult. Limited rheological properties are available for oil-water emulsion especially for heavy crude oil comprising of asphaltenes and resins. Methods such as the use of chemical Demulsifier and electro coalescence are employed but none of the methods is capable to give full or satisfactory separation. In this report, I have tried to give a brief review of rheological behavior and the techniques employed for the determination of rheological parameters. I have also tried to go through the work which has been done to understand the rheological behavior of different emulsions under various conditions. The future scope of research will involve understanding the structure and chemistry of interfacial films with respect to emulsion films and also the associated adsorption dynamics.

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