

7. SURFACE TENSION AND DETERMINATION

Surface tension is the force that must be applied to the unit length to increase the surface of a liquid by 1 cm^2 . The tension between the surfaces is called as interface tension. This has a lower value than the surface tension. Surface and interface tension is numerically equal to surface free energy. For example, the surface tension of water at 20°C is 72.8 dyn/cm ; surface free energy is 72.8 erg/cm^2 . The surface free energy can be defined as the work to be done to increase the surface by 1 cm^2 . Surface tension and interfacial tension is indicated by " γ " and the unit is " dyn.cm^{-1} " according to the CGS system and " $\text{miliNewton/meter (mN.m}^{-1}\text{)}$ " according to SI system. The surface tension changes with temperature. The surface tension shows a decrease as the temperature increases.

Various methods can be used for determine the surface and interface tensions. Some of these methods determine the surface tension only, and some are used for determine both surface and interface tension.

The main methods used are;

1. Capillary method
2. Wilhelmy plate method
3. Du Noüy ring method
4. Drop method
 - Simple dropper method
 - Donnan pipette method
 - Pendant drop method
 - Sessile drop method
5. Oscillating jet method
6. Maximum bubble pressure method

Practice 7.1

Surface Effectiveness

| | |
|----------------------|-------------|
| Surface active agent | 1 g |
| Purified water | q.s. 100 ml |

Preparation

- a) Put 10 ml of water on a tube and add 1 ml of olive oil on it. First, the tube monitored without movement. Then shaken for 1 minute and monitored again.
- b) Put another 10 ml of the solution prepared according to the above formula and then add 1 ml of olive oil. The tube monitored without movement. Then shaken for 1 minute and monitored again.

Questions:

1. Is there a difference between the states of olive oil placed on both liquids? Do you see the difference between the surface-active ingredients of olive oil and the interfaces of water-olive oil mixtures?
2. Describe the surface tension. What is surface active agent?
3. Does the difference between the appearances of the two mixtures after rinsing occur? If so, explain why.
4. Take 2 ml of each mixture. First, apply hand thoroughly from the mixture containing the surface active substance and wash. Then apply and wash the other mixture. Which mixture is easier to wash than your hand? Explain why.
5. Check the tubes you put in each mixture as you leave the lab and write the differences you see between the two blends.
6. What surface is the active substance used?

Practice 7.2

Determination of Surface Tension of a Liquid with Simple Dropper

The principle of this method is to determine the surface tension of a liquid with the aid of a number of drops, drop weight or drop volume of a known surface tension liquid aid and a based on the Hagen-Poiseuille equation. The force holding a droplet about to drop from a droplet is proportional to the droplet radius and the surface tension of the droplet. The weight of the droplet when dripping is equal to the surface tension of the liquid.

$$m \cdot g = 2\pi r \gamma ; \quad \gamma = m \cdot g / 2\pi r$$

- m : Mass of the liquid drop (g)
- g : Gravitational constant (980.7 cm.s⁻²)
- r : Dropper radius (cm)
- γ : Surface tension of the liquid (dyn.cm⁻¹)

Measurement of surface tension of the olive oil with water surface tension (72.8 dyn / cm)

A- A dropper or pipette is taken. Drop 50 drops of water with this dropper and calculate one drop of water (m₁) from this total 50 drops weight. This pot is dried and dropped 50 drops of olive oil with the same dropper and weighed again. Calculate of one drop of oil (m₂). The surface tension of the oil is calculated from the following equation.

$$\gamma_1 / \gamma_2 = m_1 / m_2$$

- γ₁: Water surface tension (dyn.cm⁻¹)
- γ₂: Surface tension of olive oil (dyn.cm⁻¹)
- m₁: mass of water (g)
- m₂: mass of olive oil (g)

B- Weigh 5 grams of water and olive oil, and determine the number of drops of each one and calculate the surface tension of the olive oil with the following equation.

$$\gamma_1 / \gamma_2 = \eta_1 \rho_1 / \eta_2 \rho_2$$

- γ₁: Water surface tension (dyn.cm⁻¹)
- γ₂: Surface tension of olive oil (dyn.cm⁻¹)
- η₁: Water drop number (5 grams)
- η₂: Olive oil drop number (5 grams)
- ρ₁: Water density (g.cm⁻³)
- ρ₂: Olive oil density (g.cm⁻³)

8. VISCOSITY AND DETERMINATION METHODS

8.1. Viscosity

Viscosity is the resistance of a liquid to flow. The larger the resistance the higher the viscosity. The flow properties of the liquids were quantitatively investigated by Newton first and it was expressed by the following equation.

$$F / A = \eta (dv / dx)$$

In this equation,

dv / dx : slip speed between two liquid layers sliding on each other
(speed gradient)

F / A : Force or slip shear per unit area to create the shear rate

η : Dynamic viscous coefficient or dynamic viscosity

According to the European Pharmacopoeia 4, “ dv / dx ” is indicated by D and “ F / A ” is indicated by τ and as a result the equation can be given as:

$$\eta = \tau / D$$

Fluids fitting to the Newtonian flow are called “Newtonian” fluids while the not fitting fluids are called “non-Newtonian” fluids. Viscosity of simple liquids such as water, glycerin, liquid paraffin can be expressed by a numerical value but non-Newtonian systems such as suspension, emulsion, cream, ointment can be expressed by the viscosity curve (rheogram).

The viscosity according to the European Pharmacopoeia 4 is denoted by “ η ” and the kinematic viscosity is denoted by “ ν ”. The dynamic viscosity is expressed in millipascal seconds (mPa.s) and the kinematic viscosity is expressed in mm^2s^{-1} . The kinematic viscosity is the value obtained by dividing the dynamic viscosity by the density and shown equation in the below

$$\nu = \eta / \rho$$

ν : Kinematic viscosity (m^2s^{-1})

η : Dynamic Viscosity (Pa.s)

ρ : Density of the liquid at a certain temperature (kg.m^{-3})

The units of dynamic and kinematic viscosities according to various unit systems are shown in Table 8.1.

Table 8.1. Viscosity coefficients for different unit systems

| Unit system | The dynamic viscosity (η) unit | The kinematic viscosity (ν) unit |
|-------------|--|--|
| SI | Pa.s | m^2s^{-1} |
| CGS | $\text{dyn.cm}^{-2} \cdot \text{s}$ | cm^2s^{-1} |
| Other | poise (P) centipoise(cP) (= 1 mPa.s) | stoke (St) centistoke(cSt) (= $10^{-4}\text{m}^2\text{s}^{-1}$) |

8.2. Viscosity Determination Methods

The principle of these methods are measuring resistance to the flow of liquid in a capillary tube or measuring the resistance of the liquid to a solid material motion in the liquid. The instruments used to determine the viscosity is classified into two main groups.

1- Instruments measuring in single point

In this group;

- Capillary viscosimeters: Ostwald viscometer, Ostwald-Cannon-Fenske viscometer, Ubbelohde tube
- Falling ball viscometer: Hoopler falling ball viscometer.

2- Multi-point measuring instruments

In this group;

- Coutte type MacMichael viscosimeter based on Rotational Cup and Bob viscometer, Searle type Haake Rotovisco viscometer, Stormer viscometer,
- Ferranti-Shirley viscometer based on rotational cone and plate viscometer., Brookfield viscometer and penetrometers.

The viscosities of both Newtonian and non-Newtonian systems can be detected with multi-point measuring instruments.

8.2.1. Viscosity Determination with Capillary Viscometer Method

By attaching a viscometer to the support material, the test fluid (liquid to be measured ~~viscous~~) is filled from L1 tube between the lines B-C and vacuum is applied from L2 tube until the fluid pulls up to line A . Then the vacuum is removed and the time for the liquid to drain from A to B (t_1) is determined. This test is repeated with a fluid of known viscosity, usually water, to determine the required time (t_2). Viscosity is calculated by applying the data to the below equation.

$$\eta_1 / \eta_2 = (\rho_1 t_1) / (\rho_2 t_2)$$

η_1 : Viscosity of the test liquid (P)

η_2 : Viscosity of water (at room temperature) (P)

ρ_1 : Density of test fluid (g cm^{-3})

ρ_2 : Water density (g cm^{-3})

t_1 : Time of passage of test liquid (s)

t_2 : Water transition time (s)

8.2.2. Determination of Viscosity by Falling Ball Method

The instrument is filled with liquid to measure the viscosity of the glass tube. One of the balls is selected and left in the pipe. The transit time (t) between the two marking lines in the pipet is determined and the viscosity (η) is calculated by the following equation.

$$\eta = t (S_b - S_f) B$$

η : Viscosity of liquid (cP)

t : Time of transition of the ball (s)

S_b : Density of the ball (g.cm^{-3})

S_f : Density of the liquid (g.cm^{-3})

B : Constant belonging to the selected ball

8.2.3. Viscosity Determination with Rotational Viscometer

The shear rate and shear stress data obtained with these viscosimeters are plotted to form a rheogram.

Fluid to be measured is put the viscometer into the container. Part of the device, which can be in the form of a cylinder, cone or rotary disk (spindle), is immersed. For example, in a Bob and Cup viscometer (Fig. 8.3), which is a type of rotational viscometer, the rotational moment generated by the fluid drag around the portion of the cylinder submerged in liquid is measured by a coil or sensor. The torque is proportional to the shear stress of the liquid.

Practice 8.1.

- 1- 3% w / v carboxymethylcellulose (CMC)
- 2- 5% w / v bentonite solution,
- 3- Liquid vaseline

Determine the viscosities of these liquids at room temperature by working with all three instruments.

Questions:

1. Draw the rheogram of each fluid at increasing rates relative to the rotation viscosimeter. Compare the results with the reasons.
2. How can you choose the viscometer according to the liquid flow type?
3. How much did you find dynamic viscosities and kinematic viscosities of liquid petroleum in your experimental temperature?
4. Describe the relationship of viscosity and temperature.
5. What kind of flow does a 5% w / v solution of bentonite show?
6. What should be taken into account in order to obtain a reliable viscosity value with the falling ball method?

11. EMULSIONS

Emulsions are homogeneous appearance heterogeneous dispersing systems formed by dispersing one of two liquids which do not mix with one another droplets with the help of an emulsifier in the other. A pharmaceutical emulsion essentially comprises water, oil and emulsifier and consists of three phases.

- Internal phase (disperse phase or dispersed phase).
- Emulsifier (emulsifier)
- External phase (dispersion medium or continuous phase)

Pharmaceutical emulsions such as classical emulsions, microemulsions, multiple emulsions and nanoemulsions, classified according to application route,

- Oral emulsions
- Topical emulsions
- Injectable (parenteral) emulsions.

In emulsion; type of emulsifier, type emulsion used with oil and water phase ratios specifies the emulsion type. Conventional emulsions with two phases are oil / water (o / w) and water / oil (o / o) type; while the three-phase multiple emulsions can be prepared in the form of water / oil / water (w / o / w) and oil / water / oil (w / o / w).

11.1. Preparation of Emulsions

Preparation method varies depending on the amount of the product and the formulation. There are three main preparing methods of the small scale production.

- Dry gum method
- Wet gum method
- Bottle method

In all three methods, the primer emulsion is essentially formed first. For primer emulsion, oil, water and gum are taken at certain ratios. The ratios are chosen according to the oil property. Ratios of 4: 2: 1, 3: 2: 1, 2: 2: 1, 1: 2: 1 (oil: water: gum) are used according to the formation of fixed oil, mineral oil, volatile oil and oleo-resin respectively.

Dry gum method: In this method, the emulsifier is added to insoluble phase, mixed rapidly, and the primary emulsion water is added in the same direction until the characteristic "snap" sound, which shows the formation of the primary emulsion. The desired volume is completed by adding the remaining aqueous phase over.

Wet gum method: In this method, the emulsifier is added to dissolved phase to form the primary emulsion. Then the remaining volume of the continuous phase is added to complete the desired volume.

Bottle method: Generally suitable for emulsion formulations containing volatile oil. For the primer emulsion, 1 k gum is taken in the bottle and 2 k volatile oil is added on it and shaken well. It is continued agitation by adding 2 k water on it. When the formation of the primary emulsion is observed, the remaining liquid phase is added and shaken.

11.3. Controls in Emulsions

1. Organoleptic controls
2. Quantification of drug content
3. Emulsion type determination
4. Determination of droplet size and size distribution
5. Viscosity

11.4. Stability Studies in Emulsions

1. Physical stability
2. Chemical stability
3. Microbiological stability

Practice 11.1.

Olive oil emulsion
Emulsio olei olivae

| | |
|----------------|-------|
| Olive oil | 8 ml |
| Arabic gum | 2 g |
| Purified water | 4 ml |
| Simple syrup | 10 ml |
| Purified water | 15 ml |

Preparation:

Put gum in a dry porcelain mortar. Olive oil is added on it and the mortar is mixed gently with hand. Add 4 ml of water all at once and mix immediately and rapidly. Continue to stir until a pronounced forming of the primer emulsion appears to sound. It is then stirred for another five minutes. 10 ml simple syrup is added slowly and mixed on. Then 15 ml of water are added again with constant stirring. It is bottled and labeled appropriately.

Questions:

- 1- What is the preparation method?
- 2- What is the pharmaceutical form of the preparation? For what purpose can it be used?
- 3- Specify the type of emulsion. By which method did you determine the type of emulsion? What is your emulsion type?