

## Module 9 : Experiments in Chemistry

### Lecture 39 : Properties and Equilibria: Viscosity and Partition Coefficient

#### Objectives

After studying the present lecture, you will be able to

- Define viscosity and viscosity coefficient.
- Outline the method to measure viscosity using Ostwald viscometer.
- Determine the average molecular weight of a polymer.
- Determine the surface concentration of 1-butanol in aqueous solution.
- Measure the distribution coefficient of a solute between two solvents.

#### 39.1 Introduction

Viscosity, one of the transport properties, arises because of intermolecular attractive and relatively long-range forces. Viscosity coefficient ( $\eta$ ), a specific constant characteristic of a liquid could be expressed by the following equation of Poiseuille.

$$\eta = \frac{P\pi r^4 t}{8LV} \quad (39.1)$$

where V is the volume of liquid delivered in time t, through a capillary of radius r and length L, with a hydrostatic pressure P.

In an apparatus designed so that equal volumes of liquids can flow through the same capillary of length L and radius r,  $\eta$  may be written as

$$\eta = k' h d g t \quad (39.2)$$

If g remains constant in any given location and h, the height through which the liquid falls is kept constant, above equation becomes,

$$\eta = k d d \quad (39.3)$$

where k is the dimensional constant of the apparatus.

If two liquids are compared using the same apparatus, it follows that

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad (39.4)$$

If  $\eta_2$ , the coefficient of viscosity of one of the substances, is known from a previous measurement, then  $\eta_1$ , the viscosity of the other liquid, can be calculated from the measured quantities,  $d_1$ ,  $d_2$ ,  $t_1$  and  $t_2$ .

#### 39.2 Viscosity measurement of a liquid

The viscosity of two liquids can be compared by making use of an Ostwald Viscometer which consists of two bulbs, one attached with a capillary tube and U-tube below the capillary tube while other bulb is attached to the other arm of U-tube at a level lower than the other bulb. The liquids of known densities are allowed to flow through the capillary maintaining the same differences of levels in the limbs and the time equation which governs the flow lead to the relation:

$$\frac{\eta_1}{\eta_2} = \frac{t_1 d_1}{t_2 d_2} \quad (39.5)$$

where  $\eta_1$  and  $\eta_2$  are viscosity coefficients of the liquid and water, respectively and  $d_1$  and  $d_2$  are the densities of

$$\eta_1 \quad \eta_2$$

liquid and water, respectively. Knowing the value of viscosity of one liquid, one can calculate the viscosity of other liquid.

The procedure for measurement of viscosity is as follows. The viscometer is fixed vertically on the stand and 10 mL or 20mL of water is pipetted into the lower bulb. The volume of water (10 mL or 20 mL) is chosen so that the liquid can be conveniently sucked into the upper bulb leaving some in the lower bulb. It is sucked up into the other bulb to a point about the mark above the bulb. Now it is released and stop clock is started when the meniscus crosses the mark. The clock is stopped when the mark below the bulb is passed. The time is recorded at the moment. The same procedure is repeated twice or thrice and their average is used in calculations.

Similarly, the experiment is repeated with the given liquid. Using the specific gravity bottle, one can determine the specific gravity of the liquid and then calculate the viscosity. The viscosity of water at room temperature is used from the tables.

### 39.3 Experiment: to determine the average molecular weight of the polymer

Viscosity of a polymer solution could be studied to determine average molecular weight of the polymer. An average molecular weight is calculated because the polymer molecules do not all have the same mass.

Empirically it has been found that the intrinsic viscosity is sensitive both to the shape and molecular weight of the macromolecular solute. The equation used by the Mark-Houwink relation is

$$[\eta] = KM^a \quad (39.6)$$

where M is the average molecular weight and K and a are constant for a given solvent-solute system. The constant a is sensitive to the shape and varies from zero for hard sphere or 0.5 for random coils to 2.0 for rigid rods.

Variation of specific viscosity of a solution  $\eta_{sp}$  (specific viscosity or reduced viscosity) is defined as

$\eta_{sp} = \frac{\eta_i - \eta_o}{\eta_o}$ , where  $\eta_i$  is the viscosity of solution i and  $\eta_o$  the viscosity of pure solvent) with the concentration of solute is given by the equation:

$$\frac{\eta_{sp}}{c} = [\eta] + Kc [\eta]^2 \quad (39.7)$$

where, c is concentration of the polymer in g/mL and K is a constant.

The determination of average molecular weight of polyvinyl acetate in acetone and methanol uses the following Procedure:

Prepare solution of polyvinyl acetate in acetone containing approximately 1 mg/ mL. From this prepare four more solutions of 0.2, 0.4, 0.6, 0.8 mg/ mL by dilution. Measure the specific viscosity of all the four solutions as described above.

Repeat the above experiment with solution of polyvinyl acetate in methanol.

Plot  $\eta_{sp}/C$  versus c and calculate  $[\eta]$  and K from equation (2). Also, using the empirical formula (1) and constant of K and a from the table given below, determine the molecular weight of polyvinyl acetate in these two solvents.

Solvent	K	a
Acetone	$21.4 \times 10^{-5}$	0.68
Methanol	$38 \times 10^{-5}$	0.59

### 39.4 Excess Surface Energy (Surface Tension)

In this experiment, we study the determination of surface concentration of 1-butanol in aqueous solution.

The addition of a surface active agent into any liquid changes the surface tension of a liquid. The change in surface tension is related to the excess surface concentration of the solution by the Gibb's adsorption isotherm:

$$\tau = -\frac{1}{RT} \cdot \frac{d\gamma}{d \ln c} \quad (39.8)$$

$$\tau = -\frac{c}{RT} \cdot \frac{d\gamma}{dc} \quad (39.9)$$

where,

$\tau$  = surface excess concentration of solute per unit area

R = gas constant

T = absolute temperature

$\gamma$  = surface tension of the solvent

c = concentration of the solute

The surface tension may be compared with that of pure liquid using a Stalagmometer which is operated on the "drop-weight" principle. The Stalagmometer has a bulb with a capillary attached and marks on either side of the bulb. We let the fixed volume of a liquid flow through the capillary and count the drops; knowing the densities of liquids, the drops weight and hence the surface tensions, may be compared:

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_2}{n_1 d_1} \quad (39.10)$$

where  $\gamma_1$  and  $\gamma_2$  are the surface tension of water and liquid.  $d_1$  and  $d_2$  are the densities of water and liquid, respectively.  $n_1$  and  $n_2$  are the number of drops of water and liquid.

#### Procedure

A 4% (v/v) solution of 1-butanol is supplied from which 3%, 2% and 1% solution of 1-butanol is prepared using dilution method. The Stalagmometer is clamped vertically. Water is sucked up into the Stalagmometer from a beaker to a level above the bulb. It is started to release and when the level crosses the mark, counting of the drops is started till the level crosses the lower mark. This experiment is repeated and the average of the reading is taken in calculation. The similar experiment is conducted with each diluted solution and their densities are determined using a specific gravity bottle. The value of  $\gamma$  is plotted against  $\ln c$  or the value of  $\gamma$  is plotted against c. From the plot, the slope at two points are found by drawing tangents at  $c = 1.5\%$  and  $c = 2.5\%$ .

The surface excess concentration of 1-butanol is calculated from the slope of the curve in each case.

#### 39.5 Distribution Coefficient

If in a system of two immiscible or slightly miscible solvent, a substance, soluble in both the solvents is added, then the added substance will distribute itself between the two liquids in a definite manner depending upon its solubility. At equilibrium the ratio of the concentrations of the solute in the two liquids is constant at a given temperature and is called the distribution coefficient or partition coefficient. It is important that the solute must exist in the two solvents in the same molecular state. If  $C_1$  and  $C_2$  are the concentrations of the solute in the two solvents when equilibrium is reached, then at constant temperature.

$$\frac{C_1}{C_2} = \text{Constant, } (K_{part}) \quad (39.10)$$

#### Experiment:

Determine the distribution coefficient of iodine between carbon tetrachloride and water at a given temperature (or room temperature).

#### Theory:

The molecular state of iodine in both the solvents  $\text{CCl}_4$  and water is the same as  $\text{I}_2$  and hence the partition coefficient is practically independent of concentration in dilute solutions. Hence, the distribution law in its simplest form may be applied i.e.,

$$C_{org} / C_{aq} = K_{part} \text{ (Partition Coefficient)}$$

**Procedure:**

1. By means of a graduated pipette place about 50, 40, 30 and 20 mL of a saturated solution in  $I_2$  in  $CCl_4$  and properly labeled (1 to 4) glass stoppered bottles. Add approximately 0, 10, 20 and 30 mL  $CCl_4$  to bottle nos. 1, 2, 3 and 4, respectively. Add about 200 mL of distilled water to each of the bottles.
2. Stopper the bottles tightly and shake thoroughly. Withdraw 20 mL of the aqueous layer carefully and titrate against 0.01 N  $Na_2S_2O_3$  using starch solution as indicator (repeat to concordance). To analyse the lower  $CCl_4$  layer, introduce a dry 5 mL pipette into the bottle while blowing continuously in and lower till the bottom is reached, withdraw 5 mL of the lower layer of  $CCl_4$  and titrate against 0.1N thiosulphate solution. Calculate the ratio of concentrations.  
Similarly, titrate aqueous and  $CCl_4$  layer from bottle nos. 2, 3 and 4 and observe that the partition coefficient is reasonably constant. Take the mean value as K part.

While titrating the non-aqueous layer, the titration flask must constantly be shaken, otherwise the equivalence point may pass without the disappearance of purple colour of non-aqueous layer. The addition of about 5mL of 10% KI solution also helps. KI facilitates extraction of iodine into aqueous solution during titration due to the formation of unstable complex ion  $I_3^-$  as  $I^- + I_2 \rightleftharpoons I_3^-$ .

**Exercise:**

Distribution of succinic acid between water and ether could also be studied. Succinic acid also remains in normal molecular state in both water and ether. Take about 1.0, 1.5 and 2.0 g of succinic acid on three stoppered bottles numbered 1 to 3. To each bottle add about 50 mL ether and 50 mL distilled water. Titrate 10 mL of ethereal layer with 0.05 M NaOH and 10 mL g aqueous layer with 0.5 M NaOH.

Calculate the concentration of the acid in the two layers in terms of moles/ l and obtain the average value of he ratio of concentrations to get K part.

**Application:**

An experiment using the distribution law is discussed below

**39.6 Determination of the equilibrium constant of the reaction**



**Theory:**

If iodine is added to a moderately concentrated aqueous solution of KI, it combines with the iodide ion to form tri-iodide ion,  $I_3^-$ . Thus, in aqueous KI solution containing iodine, we have the chemical reaction

$KI + I_2 \rightleftharpoons KI_3$  and the equilibrium constant of the reaction is,

$$K = \frac{[KI_3]}{[KI][I_2]} \text{ or } K = \frac{[I_3^-]}{[I^-][I_2]} \tag{39.12}$$

Since molecular iodine is soluble in both the aqueous and organic  $CCl_4$  phase, it obeys the distribution law whereas KI and  $KI_3$ , being the electrolytes, are insoluble in  $CCl_4$ .

**Procedure:**

Proceed as in previous exercise, but use aqueous KI solutions of different concentration in place of water. The aqueous layer will now have more  $I_2$ , so the same thiosulphate (say 0.1N) may be used to titrate the two layers. The titre of aqueous layer correspond to total of free  $I_2$  and  $I_3^-$ , and the concentration of free  $I_2$  may be calculated using the concentration in  $CCl_4$  layer and the previously determine K part. The initial I - concentration is known and since,

$$[I^-]_{initial} = [I^-]_{equal} + [I_3^-]_{equal} \tag{39.13}$$

$$\therefore [I_3^-]_{\text{equal}} = \left[ (I^-)_{\text{initial}} - \left( \frac{K_{\text{part}}}{[I_2]_{\text{org}}} \right) \right] \quad (39.14)$$

Now, using values of  $(I_2)$ ,  $(KI)$  and  $(KI_3)$  in aqueous KI layer, the equilibrium constant can be calculated.

### Recap

**In this lecture you have learnt the following**

#### 39.7 : Summary

In the present lecture, the experiments on viscosity, surface tension and distribution coefficient were described. The viscosity of two liquids was compared by making use of an Ostwald Viscometer. The use of viscosity measurement to determine the average molecular weight of a polymer was also outlined.

If in a system of two immiscible or slightly miscible solvents, a substance, soluble in both the solvents is added, then the added substance distributes itself between the two liquids in a definite manner depending upon its solubility. At equilibrium, the ratio of the concentrations of the solute in the two liquids is constant at a given temperature and is called the distribution coefficient or partition coefficient. The determination of the partition coefficient of iodine between chloroform and water was described. The partition law was also used to determine the equilibrium constant between KI,  $I_2$  and  $KI_3$ .