CHAPTER 2

Experimental Techniques
2.1 Surface Tension Measurement

Surface tension measurements were made using a K11 Krüss Tensiometer. This instrument determines the surface tension with the help of an optimally wettable probe suspended from a precision balance. The probe is either a ring or a plate. Here we used a plate known as Wilhelmy plate method. A height-adjustable sample carrier is used to bring the liquid or solution in the sample vessel into contact with the plate. A force acts on the balance as soon as the plate touches the liquid surface. If the length of the plate is known, the force measured can be used to calculate the surface tension using the following relation

\[ \gamma = \frac{F}{L \cos \theta} \]  

(2.1)

where \( \gamma \) is the surface tension, \( F \) is the force acting on the balance, \( L \) is the wetted length of the plate and \( \theta \) is the contact angle. The plate is made of roughened platinum and is optimally wetted so that the contact angle is virtually 0° such that \( \cos \theta \) has a value of approximately 1. The K11 tensiometer is first calibrated using the prescribed method described in the instrument’s manual. By calibrating the tensiometer, actually the force measuring balance is calibrated. For calibration the supplied 1g weight is used which gives an equivalent surface tension of 243.95 mN m\(^{-1}\) according to Eq. (2.1) since the length of the plate, \( L = 0.0402 \) m.
Before every use, the plate is first rinsed with acetone to remove any organic material sticking to the plate and thereafter washed with Millipore water. Finally, the plate was heated to red hot with a Bunsen burner and then cooled.

The recommended sample vessel made up of Corning glass was used for holding the liquid or solution. This sample vessel is also cleaned thoroughly with acetone and water. The dry sample vessel is also flamed off with a Bunsen burner to make it free from any surface-active substance. The solution is taken in the cooled sample vessel up to the recommended height. The sample vessel containing the solution is then placed in the steel jacket of the tensiometer. The steel jacket is maintained at the required temperature using Haake DC 10 circulation bath. The supplied temperature sensor senses the temperature of the solution. The recommended immersion speed, search speed and immersion depth were selected. The entire operation of the tensiometer is controlled by the microprocessor. The instrument is attached to a PC and the surface tension values are displayed on the monitor screen. Ten surface tension values taken at an interval of 1 second and an average of these values were displayed on the screen. This particular tensiometer has a resolution of 0.01 mN m\(^{-1}\). The reproducibility of the measured surface tension values of the solutions was found to be within ±1 mN m\(^{-1}\). A schematic diagram of the Wilhelmy Plate method is shown in Fig. 2.1.
2.2 Electrical Conductance Measurement

Conductance measurements were made at 1 kHz using Wayne Kerr B905 Automatic Precision Bridge. This LCR meter has 0.01 nS resolution and measures conductance with an accuracy of 0.05 %. It has an averaging facility and averages 2 (‘Average’ 1) to 128 (‘Average’ 9) measurements in a time span of about 670 ms to 36 s, respectively. We have used throughout the ‘Average’ 9 option. The bridge works basically on the principle of Ohm’s law. Matching currents are passed through the standard resistor and the solution under test. The corresponding two voltages produced, whose values depend upon the impedances at the standard resistor and the test solution, are measured, resolved and computed to give the desired information on the display. All functions of the instrument are under the direct control of a microprocessor. A dip-type conductivity cell having platinized platinum electrodes was used. The cell constant was determined using standard KCl solution. The desired temperature for the solution under test is maintained with the help of Haake D8 circulation bath.

2.3 Density Measurement and Weighing

The density of solutions whenever required was measured using Anton Paar DMA 5000 Density Meter.

Weighing was done with the help of a Mettler Toledo AG245 Electronic Balance.
2.4. Fluorescence measurements

Fluorescence emission intensities of probe molecule were recorded using a Hitachi F4500 FL spectrophotometer. In our studies we have used pyrene as the probe and cetylpyridinium chloride as the quencher.

2.5. Zeta potential measurements

Zeta potential measurements were carried out on a Malvern Zetasizer 3000HS instrument.

2.6. $^1$NMR studies

$^1$H NMR spectra were recorded at 25 °C on a Bruker Avance II-400 spectrometer operating at 400 MHz with TMS as the internal reference.

2.7. Small angle neutron scattering measurements

SANS experiments were carried out at the Dhruva Reactor, Bhabha Atomic Research Center, Trombay, India. The SANS diffractometer makes use of a beryllium oxide filtered neutron beam of mean wavelength ($\lambda$) 5.2 Å and the data were collected within the Q (scattering vector $Q = 4\pi\sin\theta/\lambda$, where $2\theta$ is the scattering angle) range of 0.02–0.20 Å$^{-1}$. The samples were taken in quartz sample holder of 0.5 cm path length having tight fitting Teflon stopper. The details of SANS data analysis are described in detail in Chapter 3. A schematic diagram of the SANS spectrometer at Dhruva reactor at BARC, Mumbai is shown in Fig.2.2.
Figure 2.1 - Schematic diagram of Wilhelmy Plate.
Figure 2.2 - Schematic representation of a SANS instrument.