CHAPTER-II

EXPERIMENTAL TECHNIQUES

MATERIALS AND APPARATUS USED :

2.1 MATERIALS :

The purification of all chemicals is particularly important for studies of critical phenomena, because small traces of impurities have a large effect. The purification of solvents and reagents used for experimental observations was done by taking following precautions.

WATER :

The conductivity water was obtained by redistilling distilled water from alkaline potassium permanganate in a still similar to the one described by Kraus and Dexter[67]. The precautions suggested by these authors were carefully observed. The conductivity water was protected from atmospheric impurities.

METHANOL :

Commercial methanol was dried with Calcium Sulphate and distilled using ground glass apparatus and Calcium chloride drying tube. Fieser[68] certified 99.9 percent minimum purity by this method. The fractions were collected between 64.5 $\pm$ 0.5 ^{o} and employed for preparing the mixtures.

CHEMICAL REAGENTS

Barium nitrate and Calcium nitrate tetrahydrate used were of E. Merck, 'extra pure' grade. Both were used as such without further purification only after drying over P_2O_5

2.2 APPARATUS :

THERMOSTAT :

A water thermostat precise to $\pm 0.10^{\circ}$ was constructed employing a mercury contact thermoregulator and an electronic relay. Thermostating of all the mixtures was normally done at least for about ten minutes.

PYKNOMETER

The pyknometer of Ostwald modification of sprengel[69] type having capacity 25 ml. was used (fig. 2.1a) All the weights were taken on a sensitive double pan semimicro analytical balance.

VISCOMETER :

For the measurement of viscosity of the mixtures, Ubbelohde type viscometer[70] was used. At the lower end of piptte like bulb, A (Figure 2.2) having the two marks, m_1 and m_2, is attached a capillary which terminates in a wide tube, C. The lower funnel-like end of the capillary is located on the axis of tube C and on this the suspended level is developed. Tube, C is connected by a bent tube, g, to the lower bulb, B. This bulb is open to the atmosphere through tube 1, and tube C is in such communication through 3.

Bulb B is filled with liquid through tube 1 untill the surface of the liquid lies about between marks x and y (not marked on the glass instrument). Suction is applied to tube 2, while the top of tube 3 is closed by a finger, and tube C, capillary 4, and bulb A are thus filled with liquid as

shown in Figure 2.2 (left). When tubes 2 and 3 are opened, air passes through tube 3 into C and immediately divides the liquid into two parts, as shown in Figure 2.2 (right). In this way the suspended level is developed on the lower end of capillary 4. The liquid meanwhile begins to flow out of bulb A, through the capillary. However, it does not again fill C but flows in a thin layer down its vertical wall and joins the liquid remaining in g and B. The time is determined during which the surface of the liquid drops from mark m_1 to mark m_2. The method of operation is thus as simple as can be imagined. A liquid of 20 ml. was taken in viscometer for each reading.

STOP WATCH :

In the experiments, a stop watch reading to one tenth second was employed in measuring the time flow of the solution in the viscometer. A watch was wound up tightly and then allowed to run for a definite period before being used and was always handled in a systematic manner.

GALSS APPARATUS :

Following corning glass apparatus was used; burette, beakers 250 and 100 ml capacity. Pipette and volumetric flasks of 250 ml capacity having well ground stoppers.

2.3 METHODS AND PROCEDURES :

PREPARATION OF SOLUTIONS :

Solutions were prepared at round concentrations of 0.02, 0.04, 0.06, 0.08, 0.1, 0.12 and 0.15 M at 25° in methyl alcohol + water mixtures at 0, 10, 20 and 30 % by weight of alcohol. Solutions were kept in stoppered

container to prevent evaporation.

DETERMINATION OF DENSITY :

The exact density which was required to calculate viscosities, was measured by using pyknometer of Ostwald's modification of the Sprengel [69,71]. The pyknometer was cleaned by washing well with distilled water and then successively, with a small quantity of purified acetone. A current of dry air was drawn through the tube for drying purpose.

The pyknometer, cleaned and dried, was first weighted empty. For this purpose it was suspended from the end of the balance beam by means of a double hook (Fig 2.1 b) made of copper wire. The pyknometer (Fig 2.1 a) was then filled with distilled water by attaching a piece of rubber tubing to the end B, and sucking gently while end A dips in water.

The pyknometer was then suspended in the bath by means of a wire hook and placed over bracket made from sheet of copper (Fig 2.1 c). In the sheet of metal a hole was cut, which allowed the body of the pyknometer to pass through, while the arms were resting against the ends of the hole. The length of the opening was such as to allow the pyknometer to pass so far through that the mark on the tube B of the pyknometer was just above the metal plate; and the water in the bath was adjusted to such a height that it just touched the underside of the plate. By means of such arrangement, the danger of water getting into the ends of the pyknometer tubes was avoided and the pyknometer was held

in position more securely than by hooks.

The pyknomerer was then thermostated for about 10 minutes. The amount of water was adjusted so that it filled the pyknomerer from the point of the tube A to mark on B.(Fig 2.1 a). If there was too little water, a rod or tube carrying a drop of water was placed against the end of the tube A, when water was drawn in to the pyknometer by capillarity. If there was too much water, a piece of filter paper was carefully placed against the end of A, whereby water could be drawn from the pyknometer untill the meniscus stood exactly opposite the mark on B.

The pyknometer was then removed from the bath and the outside carefully dried by means of a cloth, taking care that none of the water was expelled from the pyknometer by the heat of the hand or by the natural expansion of the liquid when the density was being determined at temperatures below that of room. When the pyknometer had taken the temperature of the balance case, it was weighed.

When the weight of the pyknometer filled with water had been determined the pyknometer was emptied and dried and filled with the liquid the density of which was required. It was placed as before in the bath at constant temperature, the liqui d was adjusted to the mark, the pyknometer dried with a cloth as before and weighed.

If the temperature at which the pykno meter is filled with water and with the other liquid is the same, then the relative density (uncorrected for the buoyancy of the air) can be calculated by the ratio of the weight of liquid (w')

to the weight of water (w); of the liquid compared with that of water at the same temperature. This is represented by

$$d't = w'/w$$

Densities of soluions were measured at 25°, 30°, 35° and 40°C temperatures.

DETERMINATION OF VISCOSITY :

Viscosity determinations were carried out by making use of an Ubbelohde type viscometer. The viscometer was rinsed with distilled water and dried with acetone. The interior glass surface was kept clean and unmarked during all measurements. 20 ml of the sample was employed for each measurement after thermostating the solution (Fig 2.3) in the viscometer itself for 10 minutes. Viscosity magnitudes of the samples were estimated using the density values in the follwing equation.

$$\eta_1 = \frac{\eta_0 d_1 t_1}{d_0 t_0}$$

in which η was the viscosity and 't' the time taken in seconds for the flow of equal volumes of experimental sample and water and suffixes 0 and 1 stood for the magnitudes of water and experimental sample respectively. In above expression the density [72] and viscosity [73] of water at temperatures 25,30,35 and 40°C used were as follows :

$$\eta_r = \frac{\eta_1}{\eta_0} = \frac{d_1 t_1}{d_0 t_0}$$

Density and viscosity of water

temp/ ^{o}c	density ($Kg.\ m^{-3}$)	viscosity ($mN\ s\ m^{-2}$)
25	997.047	0.8903
30	995.650	0.7975
35	994.036	0.7194
40	992.219	0.6531

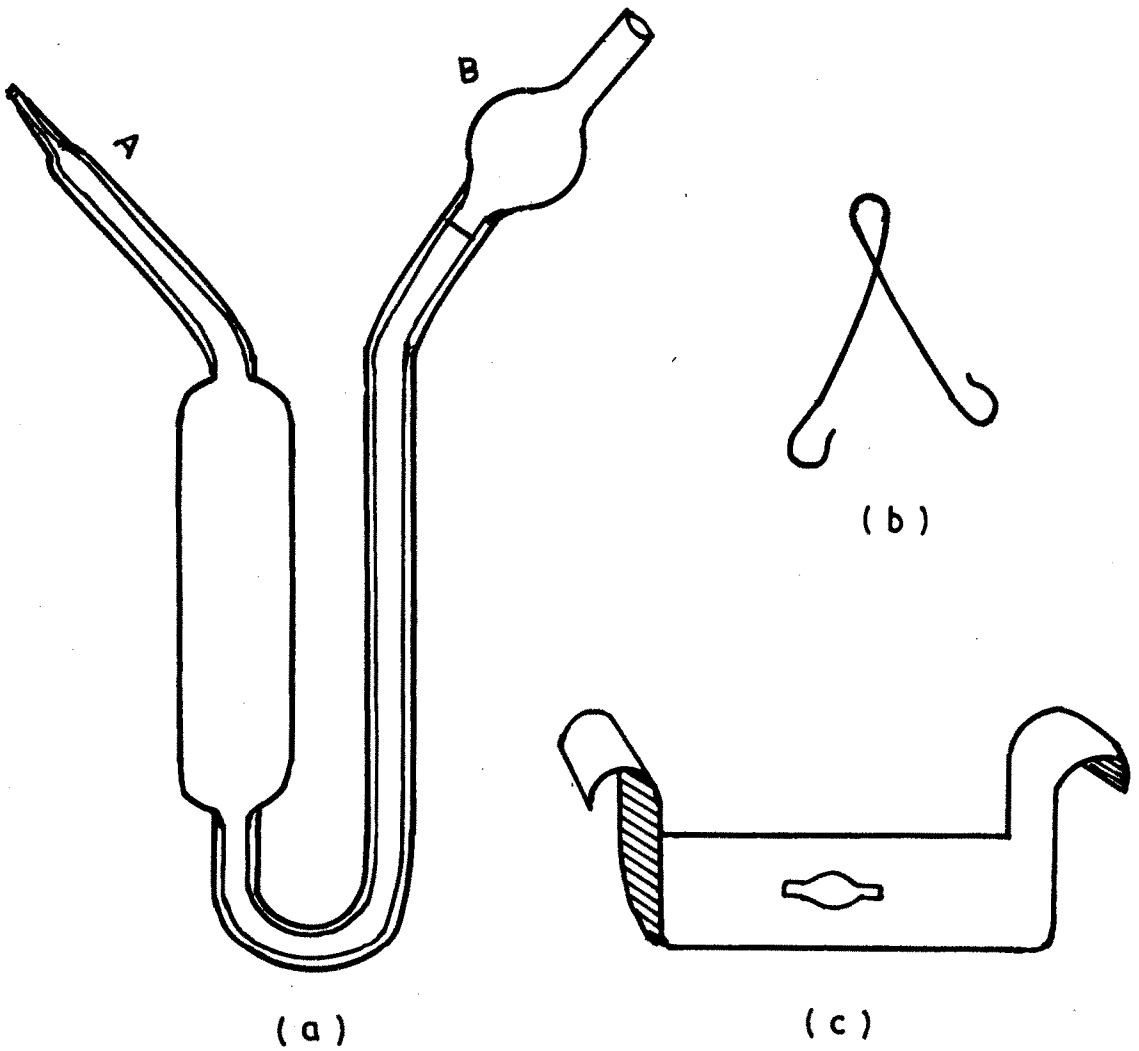

FIG. 2·1 — PYKNOMETER FOR LIQUIDS.
(a) PYKNOMETER VESSEL, (b) WIRE SUPPORT FOR WEIGHING, (c) BRACKET FOR SUPPORTING PYKNOMETER IN THERMOSTAT.

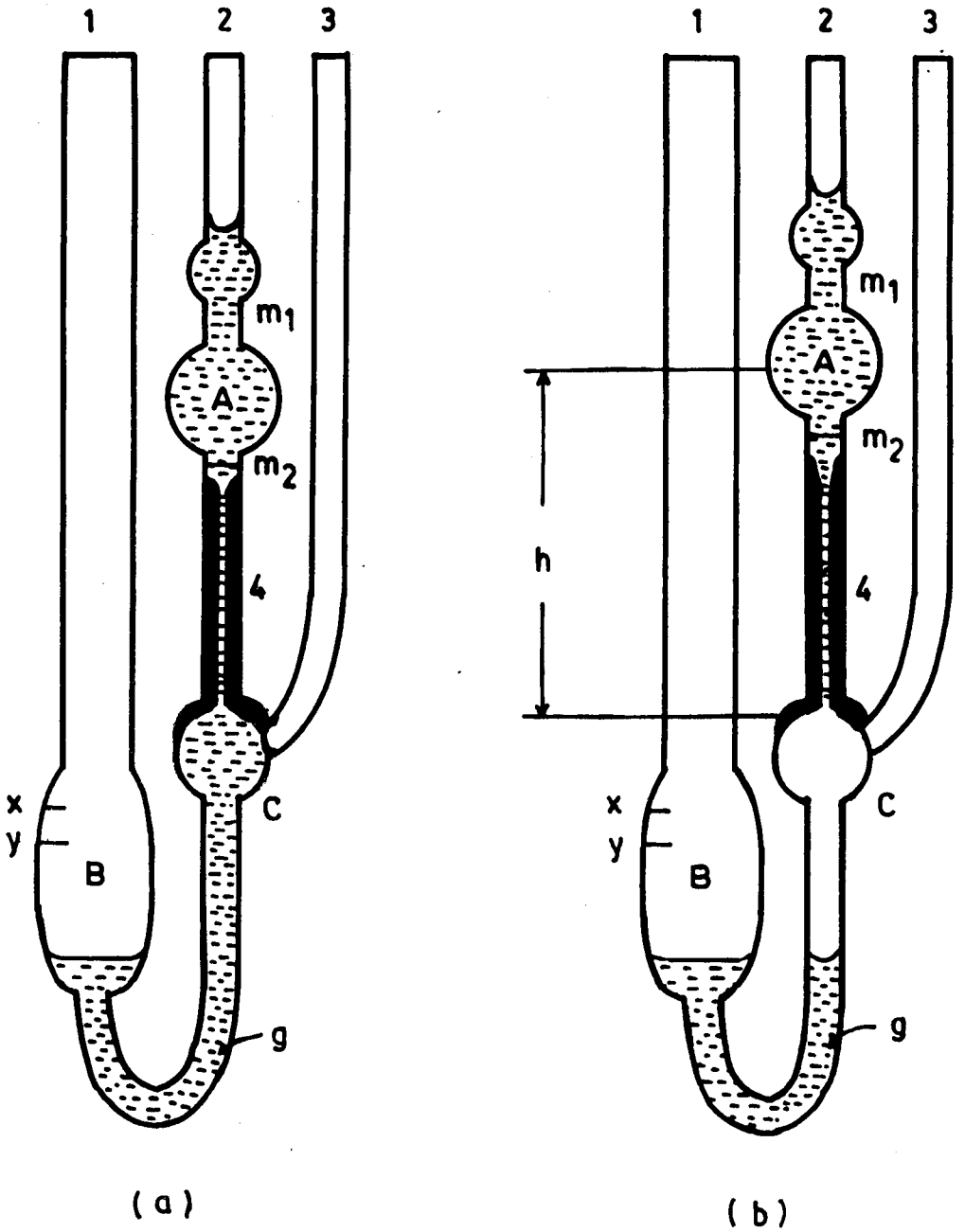

FIG. 2·2 — UBBELOHDE TYPE VISCOMETER.

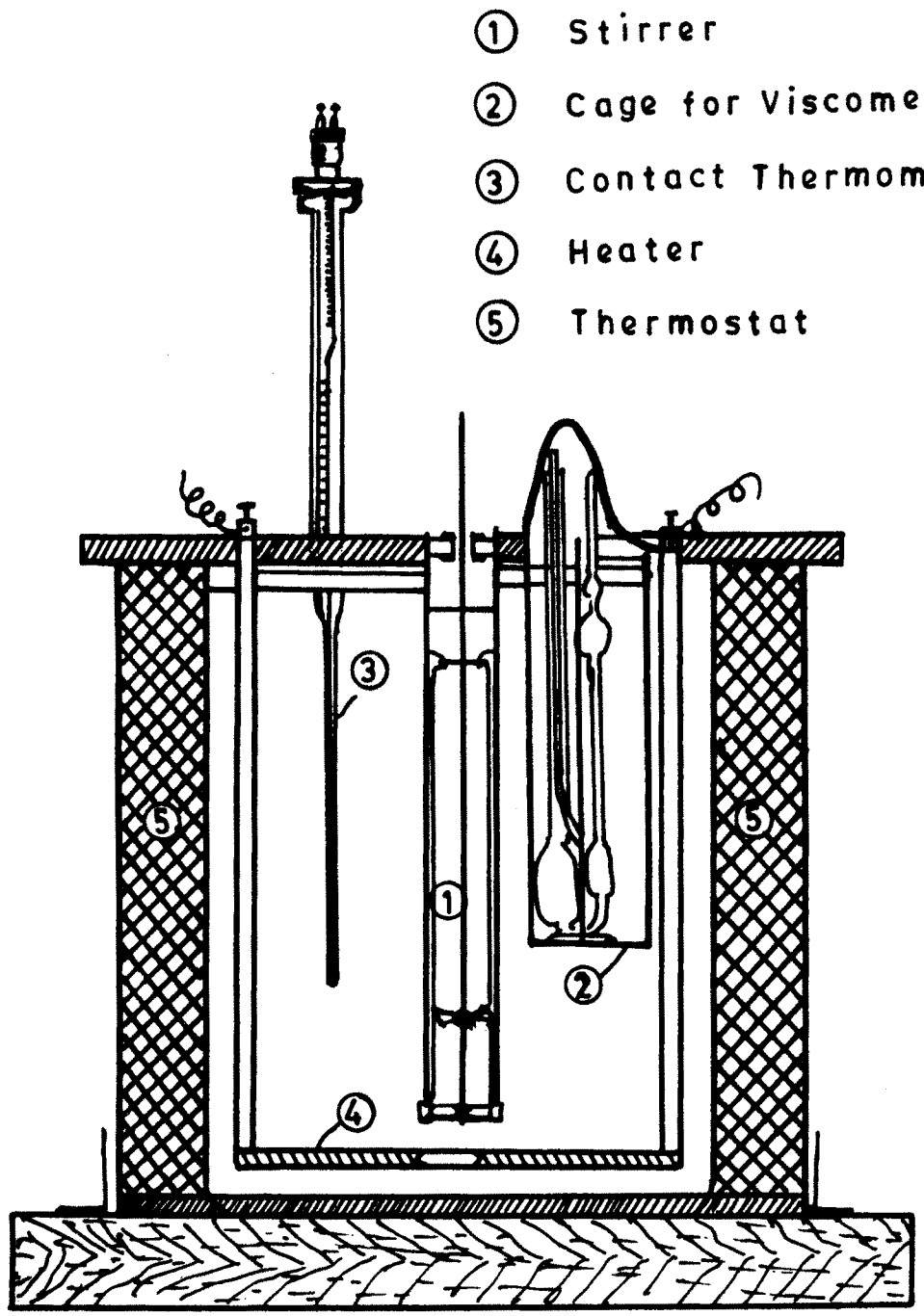

FIG. 2·3 — EXPERIMENTAL ARRANGEMENT.