Experimental
MATERIALS AND SAMPLE PREPARATION

Lactose (SD’S), Maltose (SD’S), Sucrose (BDH) and Sodium Chloride (Qualigens) used in the preparation of samples were of AR grade.

All the compounds were dried at 50°C and kept in vacuum dessicator for several hours before use. Absolute alcohol prepared from commercial alcohol (63) was mixed with triply distilled water for being used as solvent. Decimolar solutions of disaccharides as well as of sodium chloride were prepared in the said mixed solvent. Mixtures of solutions of varying composition were made on volume basis. The resulting mixture,

(a) Lactose in water-EtOH + Sodium Chloride in water-EtOH;

(b) Sucrose in water-EtOH + Sodium Chloride in water-EtOH; and

(c) Maltose in water-EtOH + Sodium Chloride in water-EtOH;

though constitute the quaternary system have been analysed like the binary ones as follows:
<table>
<thead>
<tr>
<th>Composition</th>
<th>Mole fraction $X$ of NaCl in water-EtOH</th>
<th>$V_{NaCl}^<em>$ / $V_{disacch}^</em>$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.000</td>
<td>0/100%</td>
</tr>
<tr>
<td>B</td>
<td>0.102</td>
<td>10/90%</td>
</tr>
<tr>
<td>C</td>
<td>0.204</td>
<td>20/80%</td>
</tr>
<tr>
<td>D</td>
<td>0.305</td>
<td>30/70%</td>
</tr>
<tr>
<td>E</td>
<td>0.405</td>
<td>40/60%</td>
</tr>
<tr>
<td>F</td>
<td>0.506</td>
<td>50/50%</td>
</tr>
<tr>
<td>G</td>
<td>0.605</td>
<td>60/40%</td>
</tr>
<tr>
<td>H</td>
<td>0.705</td>
<td>70/30%</td>
</tr>
<tr>
<td>I</td>
<td>0.804</td>
<td>80/20%</td>
</tr>
<tr>
<td>J</td>
<td>0.902</td>
<td>90/10%</td>
</tr>
<tr>
<td>K</td>
<td>1.000</td>
<td>100/0%</td>
</tr>
</tbody>
</table>

Molecular weights have been calculated by using the usual relations,

$$[2.1] \quad M = M_1 X_1 + M_2 X_2$$

where subscripts 1 and 2 refer to the pure components of the mixture.

**TEMPERATURE CONTROL**

A thermostated paraffin bath was used to maintain

* *solution in water-EtOH*
a uniform temperature during the course of measurements of density and viscosity. The bath consists of an immersion heater (1.5 KW), a stirrer, a check thermometer (Germany) to study the change in temperature by 0.1°, a contact thermometer, and a relay [Jumo type NT 15.0, 220V-15A (Germany)] to control the variations in temperature. The overall temperature stability was found to be within ±0.1°.

An ultrasonic interferometer (Mittals, model:M-77) was used for the measurement of sound velocity at a frequency of 4MHz in the experimental temperature range. Water from an ultrathermostat (type U-10) was circulated through the brass jacket surrounding the cell and the quartz crystal. The jacket is well insulated and the temperature of the liquid under study was maintained to an accuracy of ±0.1°.

**DENSITY MEASUREMENTS**

The density measurements have been performed by using a pyknometer. A pyknometer consists of a small bulb with flat bottom (capacity ~ 4ml ) and a graduated stem. The pyknometer was calibrated with triply distilled water. The clean and dried pyknometer was weighed and filled with the triply distilled water and again weighed. The difference
of these two weights gave the weight of water taken. Then the pyknometer was immersed in the said thermostated bath and the temperature was adjusted so as to bring the volume of water to each mark of the graduated stem of the pyknometer. The density of pure water at these temperatures corresponding to each of the marks has been computed using the relation,

\[ \rho = 1.000525 - 2 \times 10^{-5} t - 4.72 \times 10^{-6} t^2 \; \text{; (t°C)} \]

with a standard deviation of 4 ppm.

From the known mass and density of water, the volume corresponding to each of the marks of the pyknometer has been determined.

To check the reproducibility of calibration, the same process was repeated a number of times by taking different amounts of water.

The solution densities were determined by using the calibrated pyknometer. The accuracy in density measurements was found to be within ±0.0003 g cm⁻³.

**VISCOSITY MEASUREMENTS**

The viscosity measurements have been made with a
Cannon-Ubbelohde type viscometer (64, 65) shown in Fig.1.

The viscometer was well cleaned, dried and filled with triply distilled water. To avoid the adsorption of moisture all the open ends of the three arms of viscometer were fitted with calcium chloride tubes. The viscometer was then clamped vertically in the paraffin bath maintained at the experimental temperatures, and the time of fall of water was recorded.

The Poiseuille’s equation,

\[ [2.3] \eta = \frac{\pi \rho h g r^4 t}{8 L V} = \rho \beta t \]

was employed for the calculation of viscosity. The terms have their usual meaning. For example, \( \rho \) is the density, \( h \) is the height of the column in the viscometer, \( g \) is the acceleration due to gravity, \( r \) is the radius of the capillary of the viscometer, \( L \) is the length and \( t \) is the time of fall of the test liquid of volume \( V \) to fall through the capillary. The terms associated with a given viscometer have been denoted by a single term for the constant characteristic of the viscometer. The \( \beta \) values were determined by using triply distilled water at several temperatures.
Fig. 1: A Cannon-Ubbelohde Viscometer
The reproducibility of the viscosity measurement was found to be within ± 0.005 cp (≡ Kg m⁻¹ s⁻¹). The viscosities of the test solutions were measured using the calibrated viscometer by recording the time of fall at the experimental temperatures using the relation,

\[ \frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \]

where \( \eta, \rho \) and \( t \) are the viscosity, the density and the time of fall while the subscripts 1 and 2 refer to water and the test solutions, respectively.

ULTRASONIC MEASUREMENTS

INSTRUMENTATION

Working principle: An ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity in liquids with a high degree of accuracy.

The principle used in the measurement of velocity (\( u \)) is based on the accurate determination of the wave length (\( \lambda \)) in the medium. Ultrasonic waves of known frequency (\( f \)) are produced by a quartz plate fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz plate. If the
separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium.

This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum.

If the distance is now increased or decreased and the variation is exactly one-half wavelength ($\lambda/2$) or multiple of it, anode current again becomes maximum. From the knowledge of the wavelength, the velocity can be obtained by the relation,

$$[2.5] \quad \text{velocity} = \text{wavelength} \times \text{frequency}$$

$$u = \lambda \times f$$

**Description:**

The ultrasonic interferometer consists of two parts, (1) The high frequency generator and (2) the measuring cell.

The "high frequency generator" is designed to excite the quartz plate fixed at the bottom of the measuring cell at its resonant frequency to generate the ultrasonic waves
in the experimental liquid filled in the "measuring cell". A micrometer to observe the change in current and two controls for the purpose of the sensitivity regulation and initial adjustment of micrometer are provided on the panel of the high frequency generator.

The "measuring cell" is a specially designed double walled cell for maintaining constant temperature of the liquid during the course of measurement. A fine micrometer screw has been provided at the top which can lower or raise the reflector plate in the liquid in the cell through a known distance. It has a quartz plate fixed at its bottom.

**Adjustment of Ultrasonic Interferometer**

Instrument was adjusted in the following manner:

(1) The cell was inserted in the square base socket and clamped to it with the help of a screw provided on one of its sides.

(2) The kurled cap of the cell was unscrewed and removed from the double walled construction of the cell. In the middle portion of it the experimental liquid was poured and the kurled cap was screwed.
(3) Water was circulated through the chutes in the double wall construction in order to maintain the desired temperature.

(4) The cell was connected with the high frequency generator by a co-axial cable provided with the instrument.

For the initial adjustment two knobs are provided on the high frequency generator, one is marked with 'Adj' and the other with 'Gain'. With the knob marked 'Adj' the position of needle on the ammeter was adjusted and the knob marked 'Gain' was used to increase the sensitivity of instrument for greater deflection. The ammeter was used to record the maximum deflection by adjusting the micrometer.

**Measurements**

The measuring cell was connected to the output terminal of the high frequency generator through a shielded cable. The cell was filled with the experimental liquid before switching on the generator. The ultrasonic waves of 4MHz frequency produced by a gold plated quartz crystal fixed at the bottom of a cell are passed through the medium and are reflected by a movable plate and the standing waves are formed in the liquid in between the reflector
plate and the quartz crystal. Acoustic resonance due to these standing waves gives rise to an electrical reaction to the generator driving the quartz plate and the anode current of the generator becomes maximum. The micrometer screw was raised slowly to record the maximum anode current. The wavelength was determined with the help of total distance moved by the micrometer for twenty maximum readings of the anode current. The total distance \( d \) gives the value of wavelength with the help of the relation, 
\[
d = n \left( \frac{\lambda}{2} \right),
\]
where \( n \) is the maximum number of the readings. Once the wavelength was known the sound velocity in the liquid can be calculated with the help of relation given by eq. [2.5]. The accuracy in velocity measurements was within \( \pm 0.15\% \).

**Precautions**

(i) The generator was switched on after filling the cell by the experimental liquid.

(ii) The experimental liquid was removed out of the cell after use.

(iii) The micrometer was kept open at 25 mm. after use.
(iv) The sudden rise or fall in the temperature of circulated liquid was avoided to prevent thermal shock to the quartz crystal.

(v) While cleaning the cell care was taken not to spoil or scratch the gold plating on the quartz crystal.

(vi) The generator was given 15 seconds' warming up time before recording readings.