CHAPTER - II

EXPERIMENTAL :

2.1.1 Technique of Sound Velocity Measurement :

In the present work, for measurement of sound velocity, interferometric method is adopted which is a modified version of Owens and Simons.[38]

In this instrument ultrasonic waves of known frequency (ν) is produced by quartz crystal fixed at the bottom of the cell. These waves are reflected by movable metallic plate kept parallel to the quartz crystal. If the seperation between these two plates is exactly a whole number multiple of the sound waves length then standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and anode current of the generator becomes maximum.

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

$$u = \nu \cdot \lambda \qquad \text{----------} \quad (4)$$

The interferometer consists of two main parts.

i) High Frequency Oscillator and
ii) Measuring Cell

i) High frequency oscillator :

It is fixed at the bottom of the measuring cell, is designed to excite the crystal at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the measuring cell. A micrometer to observe the change in current and to control for the purpose of sensitivity regulation and initial adjustment of generator. The frequency was checked periodically using a frequency meter or oscilloscope.

ii) The measuring cell :

It ~~wa~~is a specially designed double wall cell for maintaining constant temperature of the liquid during experiment. Figure 4 shows the construction of the cell.

The source of the sound, a gold plated quartz crystal Q is situated at lower part of the cell, which is cylindrical. The lower surface of the quartz is metallized. A spring F acting through an interposed ring of metal, presses the quartz against the foil. The reflecting plate R, may be

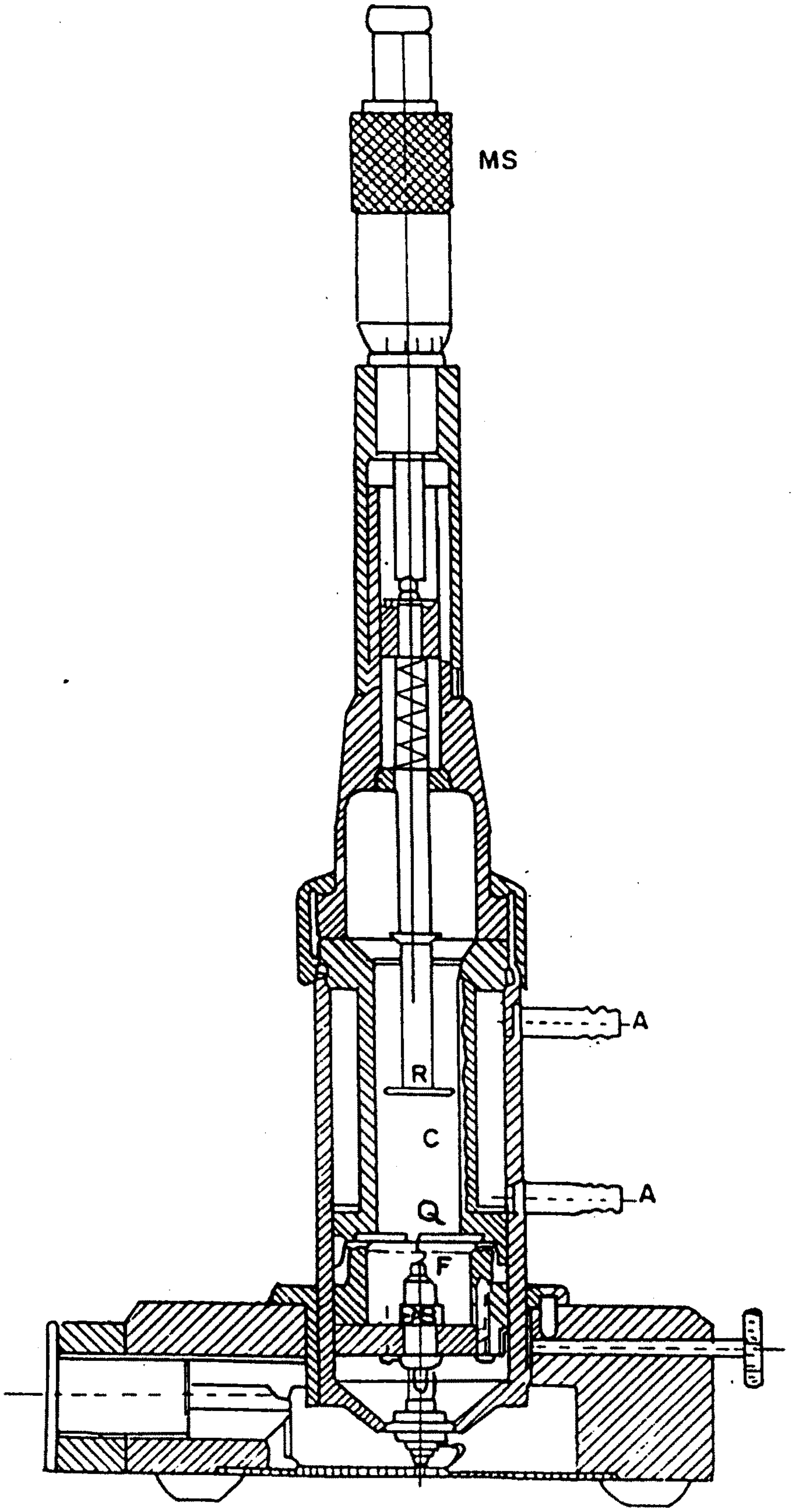

Fig.4 . Interferometer cell

displaced by means of a micrometer screw MS readable to 0.0001 cm.

The block diagram of the ultrasonic interferometer assembly for the measurement of sound velocities of all the liquids and solutions in shown in figure 5.

2.1.2 Measurements of Sound Velocity :

The measuring cell was connected to an output terminal to the high frequency generator through a shielded cable. The cell was filled with experimental liquid before switching on generator. The ultrasonic waves move normal from the quartz crystal, till they were reflected back from the reflector, and the standing waves were formed in the experimental liquid in between the reflector and quartz crystal. The micrometer screw was slowly moved till the anode current on the meter of the high frequency generator shows a maximum. A number of maxima readings of anode current were passed and their number was counted. The total distance (d) provided the value of wavelength (λ) with the help of the following relation :

$$d = n.\lambda/2 \qquad \text{----------} \quad (5)$$

Once the wavelength (λ) is known the velocity (u) in the

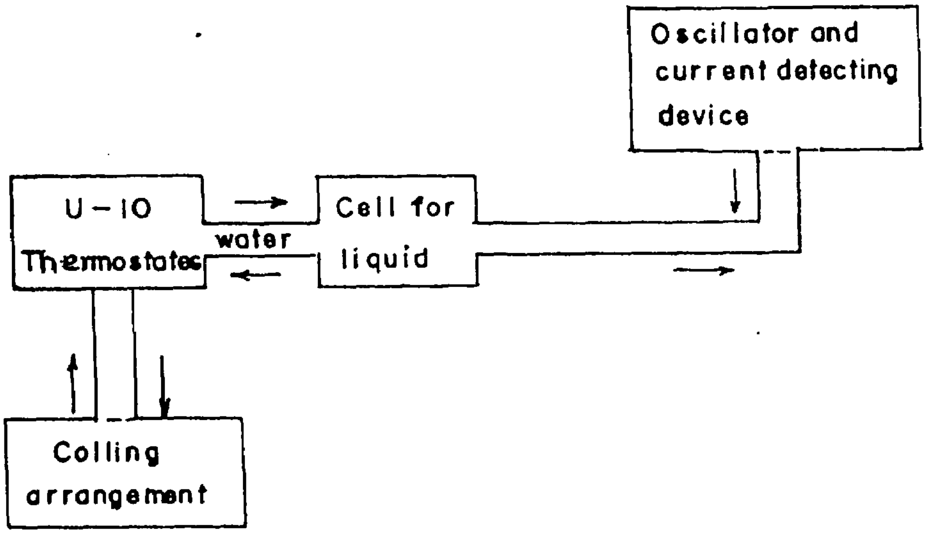

Fig.5. Block diagram of ultrasonic interferometer assembly

liquid is calculated. This method is simple and reproducible, hence ultrasonic velocity can be determined with a high degree of accuracy.

2.1.3 Accuracy and Precision of Measured Sound Velocities in the Present Work :

The interferometer cell containing sample liquid or solution was kept at constant temperature of 25°C ± 0.1° C by circulating water through it by means of assembled thermostate. The micrometer screw was calibrated by measuring $\lambda/2$ over the whole range and the best reproducible part was selected.

For the purpose of illustration, three sets of data for water, carbontetrachloride, N,N-dimethylformamide, and methanol at 25°C are collected in tables I, II, III and IV respectively. For each liquid or solution, the measurements were repeated atleast thrice. In table V measured and literature values of sound velocity are compared.

Table I : **Sound Velocity Measurements for Water at 25^{o}C**

Frequency = 2 MHz

Number of Current Maxima	Micrometer Screw Reading	20 $\lambda/2$ cm	Mean $\lambda/2$ cm	Velocity (u) m/s
20 - 0	1.0463 - .2972	0.7491	0.74898	1497.96 ± 0.5
21 - 1	1.0835 - .3346	0.7489		
22 - 2	1.1211 - .3721	0.7490		
23 - 3	1.1587 - .4096	0.7491		
24 - 4	1.1961 - .4470	0.7491		
25 - 5	1.2334 - .4847	0.7487		

The standard deviation σ was calculated by using the expression

$$\sigma = \sqrt{\frac{\Sigma (X - \bar{X})^2}{n}}$$

Where n is number of observations

X is reading from table and

$\bar{X}$ is the average of the observation.

Table II : **Sound Velocity Measurements for Carbontetracholoride at 25°C.**

Number of Current Maxima	Micrometer Screw Reading	20 λ/2 cm	Mean λ/2 cm	Velocity (u) m/s
20 - 0	0.7052 - 0.2455	0.4597	0.46035	920.7
21 - 1	0.7282 - 0.2688	0.4594		
22 - 2	0.7524 - 0.2918	0.4606		
23 - 3	0.7751 - 0.3145	0.4606		
24 - 4	0.7988 - 0.3375	0.4613		
25 - 5	0.8208 - 0.3603	0.4605		

Table III : **Sound Velocity Measurements for N,N-dimethylformamide at 25°C.** Frequency = 2 MHz

Number of Current Maxima	Micrometer Screw Reading	20 λ/2 cm	Mean λ/2 cm	Velocity (u) m/s
20 - 0	1.0451 - 0.3155	0.7296	0.72966	1459.32 ± 1
21 - 1	1.0817 - 0.3520	0.7297		
22 - 2	1.1181 - 0.3886	0.7295		
23 - 3	1.1546 - 0.4252	0.7294		
24 - 4	1.1912 - 0.4613	0.7299		
25 - 5	1.2275 - 0.4976	0.7299		

Table IV : Sound Velocity Measurements for Methanol at 25°C

Frequency = 2 MHz

Number of Current Maxmia	Micrometer Screw Reading	20 λ/2 cm	Mean λ/2 cm	Velocity (u) m/s
20 - 0	0.8285 - 0.2746	0.5539	0.55385	1107.7 ± 1
21 - 1	0.8565 - 0.3034	0.5531		
22 - 2	0.8840 - 0.3300	0.5540		
23 - 3	0.9117 - 0.3576	0.5541		
24 - 4	0.9397 - 0.3856	0.5541		
25 - 5	0.9673 - 0.4134	0.5539		

Table V : Sound Velocity for different liquids used at 25°C along with literature values.

Liquids	Velocity $m.s^{-1}$	
	Experimental	literature[39,40]
Water	1498	1497.5
Carbontetrachloride	920.7	923
DMF	1459.3	1459
Methanol	1107.7	1103

2.2.1 Measurement of Density :

In the present work, densities of all solutions were determined by a high precision Anton PAAR (Model DMA 602)[*41] digital readout densimeter. This is the most convienient and accurate method for measurement of density. In this method the measurement of natural vibrational frequency of the tube, containing liquid under investigation is made. The natural vibrational frequency of the tube is related to the density of the liquid by :

$$d = A + B.\xi^2$$

Where d = density of liquid under investigation.

A,B = Instrumental constants.

ξ = Oscillation period.

2.2.2 Experimental Procedure :

This instrument contains two units.

1. Sample holder unit
2. Reading display unit

Both units are switched on seperately. These units are connected to each other by an electric cord.

The sample tube starts to oscillate as soon as the instrument is switched on. It is therefore, ready for use. For filling of sample tube illumination for the sample tube must be on. When the illumination is turned on, the photoelectronic part of the oscillation system will not operate and density measurement is suspended. A few seconds after the illumination is turned off the instrument is again ready for measurement.

The filling of the oscillator is facilitated by the syringe holder. While loading vibrating tube with sample liquid, one has to make sure that the introduction of the liquid takes place slowly enough to enable the sample liquid to properly wet the walls of the sample tube. The meniscus of the water while filling the tube should be concave and not convex, to avoid trapping of micro air bubbles on the wall of the sample tube, which would present stable period readings.

The sample tube is completely filled when the liquid meniscus has passed the upper enlarged portion of the sample tube. The opening of the upper part of the sample tube is to be closed off with a taflon stopper and the illumination is to be turned off.

Once the illumination of the sample tube is off, vibrating tube will start oscillating and the reading of

ξ (Tau) will be displayed on the display unit after the interval of selected time period (K).

Temperature equilibration can be conveniently followed over several readout cycles until the ξ -value becomes constant ($\pm 1 \times 10^{-6}$), indicating complete temperature equilibration. At this time, value of ξ is to be selected.

ξ (Tau) is a time cycles which is related with density in following equation.

$$d = A + B.\xi^{2} \qquad \text{----------} \quad (6)$$

Where A,B are mechanical system constants.

ξ is selected readings from display unit.

Values of A and B are to be evaluated with two standard samples whose densities are known at particular temperature.

2.2.3 Calculation of A and B constans and calib~~e~~ration of the "PAAR DMA 602" densimeter :

For this instrument thermostat was attached to the sample holder unit. Temperature control was upto ± 0.05°C. Thermometer, which was used for the temperature control, was calibrated with platinum resistance thermometer and the $\overset{u}{\text{fl\cancel{a}ctuations}}$, in temperature, were being monitered by Beckman thermometer. Water with constant temperature 25°C ± 0.05°C was allowed to pass through the sample holder unit with a control speed of 6 lit./min. 2K, 5K, and 10K time cycles were selected for the calib~~e~~ration of instrument. Air and Double distilled water were used as standard samples for measurements. ξ values, at 5K of water and Air were calculated several times.

Table VI shows the readings of air and water and the calculations of A and B. Using the equations, as shown in the table VI, values of A and B were calculated.

Table VI : Calculations and Values of A and B constants at 5K time scale.

Sample	τ at 5K	τ(mean)	Density at 25°C gm/cc
Water	1.683589	1.6835898	0.997047
	1.683589		
	1.683590		
	1.683590		
	1.683591		
Air	1.286260	1.2862588	0.00114
	1.286259		
	1.286259		
	1.286259		
	1.286258		

$$\text{d-Air} = A + B.\tau^2$$

$$\text{d-water} = A + B.\tau^2$$

$$0.00114 = A + B\,(1.2862588)(1.2862588).$$

$$0.997047 = A + B\,(1.6835898)(1.6835898).$$

$\therefore$

$A = -1.3963322$ at 25°C and 5K.
$B = \ \ 0.8439798$ at 25°C and 5K.

These A and B constants are temperature dependent. In this study A and B were calculated at 25°C and 5K time scale.

These constants were used for the density calculations of all samples. The instrument was further calibrated with NaCl and KCl solutions. It was observed that the density values were in good agreement with literature values. Figure 6, shows the graph of 1000(d-do) vs molality of NaCl alongwith the literature data.[42]

2.2.4 Accuracy of the Instrument :

Accuracy of the instrument depends on temperature control because instrumental constants A and B are temperature dependent. As temperature control of the thermostateis upto ± 0.01° C the accuracy of the density is upto 5×10^{-6} g/cm^3. But we claim the accuracy of 1×10^{-5} g/cm^3 in the present work.

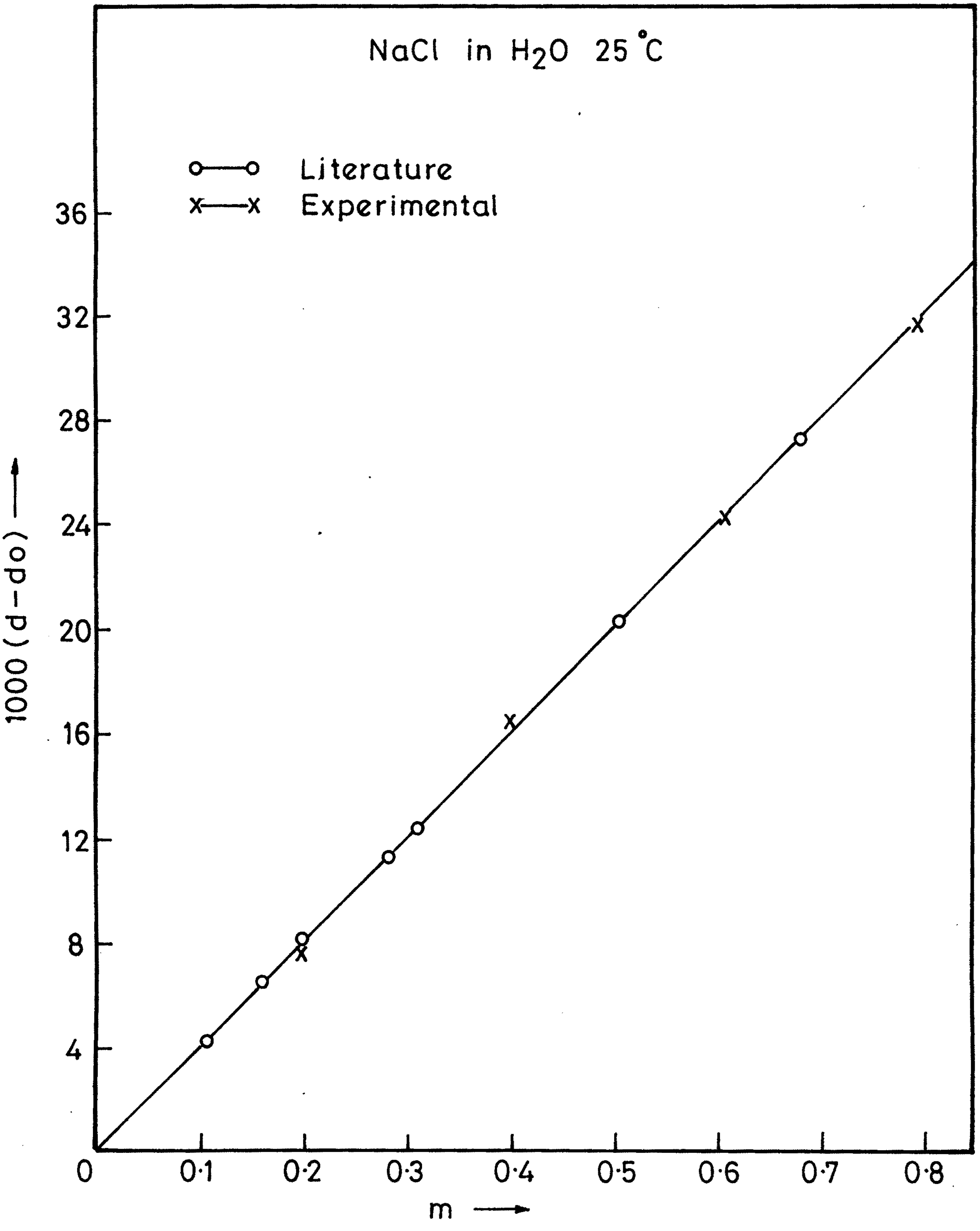
NaCl in H_2O 25 °C
Literature
Experimental
36
32
28
24
20
16
12
8
4
1000 (d−do)
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
m

Fig.6

2.3 Chemicals used :

The compounds used in this work were sodium chloride (BDH), potassium chloride (BDH) and tetrabutyl ammonium bromide (LOBA).

All the compounds were of AR grade, and were dried in a vacuum oven for 10-12 hours at 110 °C or at 60 °C and further kept in a vacuum desiccator before use. They were then used directly without any purification.

N,N-dimethylformamide, carbon tetrachloride and methanol were AR grade reagents and used directly for the measurements of density and sound velocity.

All the solutions were prepared freshly in doubly distilled water. All the measurements of electrolytes in water were done with freshly prepared solutions on molality basis. The binary solutions of DMF in water were prepared on molality basis (0 to 1 mole fraction (X_2) of DMF). The ternary solutions were prepared by varying the concentrations of salts keeping the concentration of DMF solution constant.

For weighing, one pan balance (accuracy ± 0.05 mg) was used. Then density and sound velocity measurments were made by using digital densimeter and ultrasonic interferometer respectively. The reproducibilities in the measurements of sound velocity and density were of the order of ± 0.5 ms^{-1} and ± 1 x 10^{-5} $g.cm^{-3}$ respectively.

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