CHAPTER III

3.1. Source and Purification of the Chemicals Used

3.1.1. Solvents

In this research work we have used different aqueous solutions as solvents. De-ionized water was collected from a de-ionization plant of the university of North Bengal and then it is doubly distilled in an all glass distilling set (fig. 3.1) along with alkaline $KMnO_4$ solution to remove any organic matter therein. The doubly distilled water had specific conductance of $<10^{-6}$ $S.cm^{-1}$ at 298.15 K [1]. For preparing aqueous solutions this doubly distilled de-ionized water was used. During the preparation solid-liquid solvent systems required mass of the solid component was mixed with required mass of the liquid component with necessary adjustments to achieve exact mass fraction of the solid component in the mixed solvent system [2]. During all the mixing processes adequate precautions were adopted to prevent contamination from CO_2, moisture and other impurities. The relative error in solvent composition was estimated to be about 1%.

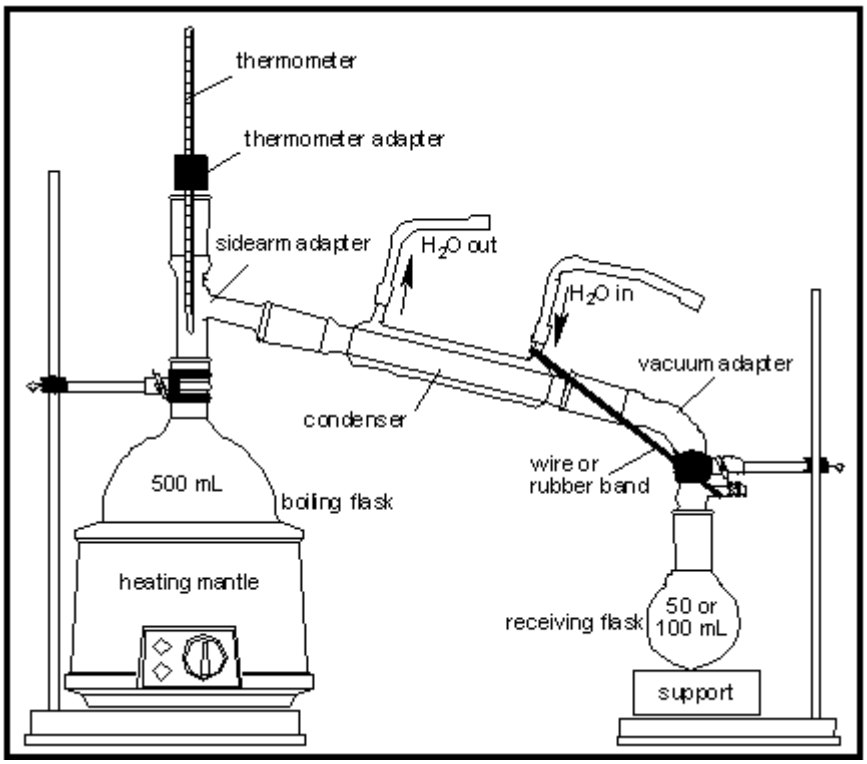

Fig. 3.1. Schematic representation of the water distillation set.

Experimental Section

A number of cosolutes were used to make the mixed solvents. Provenance and purity of these cosolutes are given in table 3.1.

Table 3.1. Provenance and purity of the cosolutes used.

Chemical	Source	Purification method	Mass fraction purity	CAS No
Tetrabutylammonium hydrogen sulphate	S. D. Fine Chemicals, India	Recrystalization	>0.985	32503-27-8
Silver sulphate	Loba Chemie, India	Recrystalization	>0.998	10294-26-5
Tributylmethyl phosphonium methyl sulphate	Sigma-Aldrich, Germany	None	>0.950	69056-62-8
L-ascorbic acid	Sigma-Aldrich, Germany	None	>0.990	50-81-7
Sodium malonate	Sigma-Aldrich, Germany	None	>0.970	141-95-7
Uracil	Sigma-Aldrich, Germany	None	>0.990	66-22-8
D-Glucose	Sigma-Aldrich, Germany	None	>0.990	50-99-7

Tetrabutylammonium hydrogen sulphate was purified by dissolving it in a 1:1 (v/v) methanol and ethanol mixture and recrystallized from diethyl ether. After filtration the salt was dried in *vacuo* for few hours and its melting point was found to be 444 K [3]. Silver sulphate was recrystallized from concentrated sulfuric acid, cooled, then diluted with de-ionized water, and the precipitate was filtered, washed, and dried at 418 K [4]. The ionic liquid tributylmethyl phosphonium methyl sulphate was used without further purification. Keep in mind the water sensitivity property of IL, a glove box was used to handle the IL; which reduces the chance of further water absorption from atmosphere. The water content in the IL was measured using a Karl-Fisher Tritaror (Veego-Matic-III, India) [5]. Water content was found 50ppm and the changes in concentration of the aqueous solutions of the IL were found within uncertainty limit of molality. Ascorbic acid, sodium malonate, Uracil and D-glucose were used as such but stored in *vacuo* over anhydrous $CaCl_2$ for several hours before use.

Stock solutions of the solutes, i.e., food additives and drugs in different aqueous solvents were prepared by mass and the working solutions were prepared by mass dilution. Solute molalities (*m*) were converted into molarities (*c*) by using experimental density values. All solutions were prepared afresh and degassed with dry nitrogen before use. The uncertainty in molality (*c*) of the solutes in solutions was evaluated to be ±0.0001 mol.kg^{-1}.

3.1.2. Solutes

A number of food additives and drugs are used as solutes for this research work. Provenance and purity of these chemicals are given in table 3.2.

Table 3.2. Provenance and purity of the food additives and drugs used.

Chemical	Source	Purification method	Mass fraction purity	CAS No
L-ascorbic acid	Sigma-Aldrich	None	>0.990	50-81-7
Thiamine hydrochloride	Sigma-Aldrich	None	>0.990	67-03-8
Nicotinic acid	Sigma-Aldrich	None	>0.995	59-67-6
Pyridoxine hydrochloride	Sigma-Aldrich	none	>0.980	58-56-0
L-Alanine	S. D. Fine Chemicals, India	Recrystalization	>0.985	56-41-7
Glycine	Sigma-Aldrich	None	>0.985	56-40-6
Lactose monohydrate	Sigma-Aldrich	None	>0.980	64044-51-5
Paracetamol	Sigma-Aldrich	None	>0.990	103-90-2
Betaine hydrochloride	Sigma-Aldrich	None	>0.990	590-46-5
Metformin hydrochloride	HiMedia Chem. Pvt. Ltd	None	>0.985	1115-70-4

L-ascorbic acid, thiamine hydrochloride, pyridoxine hydrochloride, glycine, lactose monohydrate, paracetamol, betaine hydrochloride and metformin hydrochloride were used without further purification but it was dried in *vacuo* over anhydrous $CaCl_2$ for

several hours before use. Nicotinic acid was used as received from the vendor and its melting point was found to be 534.65 K [3]. L-alanine was purified by re-crystallizing from a methanol-water mixture and dried at 373.15 K for 12 h in an infrared drier and then in vacuo over P_2O_5 at room temperature [4].

3.2. Experimental Methods

3.2.1. Mass measurement

Mass measurements were made on digital electronic analytical balance (Mettler Toledo, AG 285, Switzerland) as shown in figure 3.2.

Fig. 3.2. Digital electronic analytical balance (Mettler Toledo, AG 285).

It can measure mass to a very high precision and accuracy. The weighing pan is inside a transparent enclosure with doors so that dust does not collect and any air currents in the room do not affect the balance's operation. The electronic analytical balance measured mass with an uncertainty of $\pm 1 \cdot 10^{-4}$ g.

3.2.2. Density measurement

The density was measured with the help of Anton Paar densitometer (DMA 4500M) as shown in figure 3.3. In the digital densitometer, the mechanic oscillation of the U-tube is electromagnetically transformed into an alternating voltage of the same frequency. The period of oscillation (τ) can be measured with high resolution and stands in simple relation to the density (ρ) of the sample in the oscillator [6]:

$$\rho = A\tau^2 - B \qquad (3)$$

where A and B are the respective instrument constants of each oscillator.

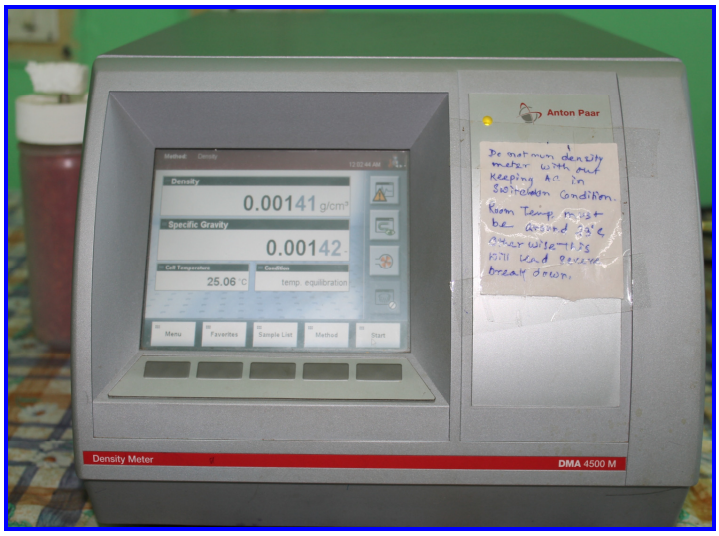

Fig. 3.3. Anton Paar densitometer (DMA 4500M).

Their values are determined by calibrating with two liquids of precisely known densities ρ_1 and ρ_2. The densities of the two liquids that are used for special adjustment have to differ by at least $\Delta\rho = 0.01\ \mathrm{g.cm^{-3}}$ and τ values of the adjustment media have to differ by at least 0.0001. Modern instruments calculate and store the constants A and B after the two calibration measurements mostly performed with air and water. They employ suitable measures to compensate various parasitic influences on the measuring result, e.g., the influence of the sample's viscosity and the non-linearity caused by the measuring instrument's finite mass.

The densitometer was calibrated at the experimental temperatures with doubly distilled, degassed water and dry air at atmospheric pressure. The temperature was kept constant with an accuracy of $\pm 1\times10^{-2}\ \mathrm{K}$ by using an automatic built–in Peltier technique. The stated repeatability and accuracy of the densities were $\pm 1\times10^{-5}\ \mathrm{g\cdot cm^{-3}}$ and $\pm 5\times10^{-5}\ \mathrm{g\cdot cm^{-3}}$, respectively. However, when the accuracy of the measured densities was tested with the density of an aqueous NaCl solution of known molality using the data given by Pitzer [7], the estimated uncertainty of the density measurements for most of the solutions was found to be better than $\pm 2\times10^{-5}\ \mathrm{g\cdot cm^{-3}}$.

3.2.3. Measurement of Viscosity

The kinematic viscosities were measured by means of capillary viscometers: a suspended-level Ubbelohde viscometer and Cannon type Ubbelohde viscometer. The

time of efflux of a constant volume of the experimental liquid through the capillary was measured with the aid of a digital stopwatch capable of measuring times accurate to ± 0.01s. The viscometer was always kept in a vertical position in the thermostatic bath with an accuracy of ± 0.01 K of the desired temperature. After attainment of thermal equilibrium, the flow times of pure liquids and liquid mixtures were measured thrice and the average of the readings was taken into account. During the measurements adequate precautions were taken to minimize evaporation loses. The efflux time for water at 298.15 K was measured to be 428.9 s. Viscosity of a solution (η) is obtained from the following equation [8],

$$\eta = (Kt - L/t)\rho \qquad (4)$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The values of the constants K and L, determined by using water and methanol as the calibrating liquids, were found to be 1.9602×10^{-3} and 4.2019 respectively. The kinetic energy corrections were done from these values and they were found to be negligible. The uncertainty in viscosity measurements, based on our work was within $\pm 0.003 \text{mPa}\cdot\text{s}$. Figure 3.4 depicts the capillary viscometers used for measuring viscosities of the solutions studied.

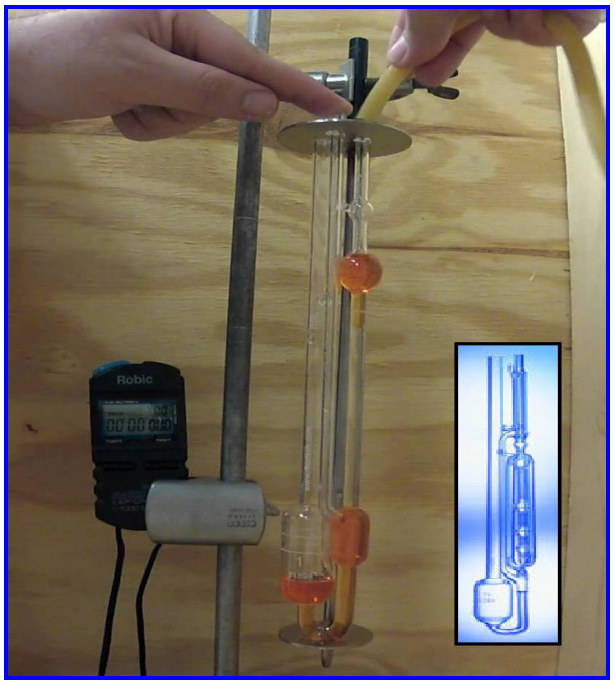

Fig. 3.4. Capillary viscometers: A suspended-level Ubbelohde viscometer. Inset: Cannon type Ubbelohde viscometer.

3.2.4. Refractive index measurement

Refractive indices were measured with an Abbe-refractometer (Cyberlab, MA01527, USA) against Sodium D light at 298.15 K. Water was circulated through the refractometer from a thermostatic bath maintained to ± 0.01 K of 298.15 K. It was calibrated by measuring the refractive indices of doubly distilled, degassed water at 298.15 K. The uncertainty in refractive indices was within ± 0.0002. Figure 3.5 shows the refractometer used.

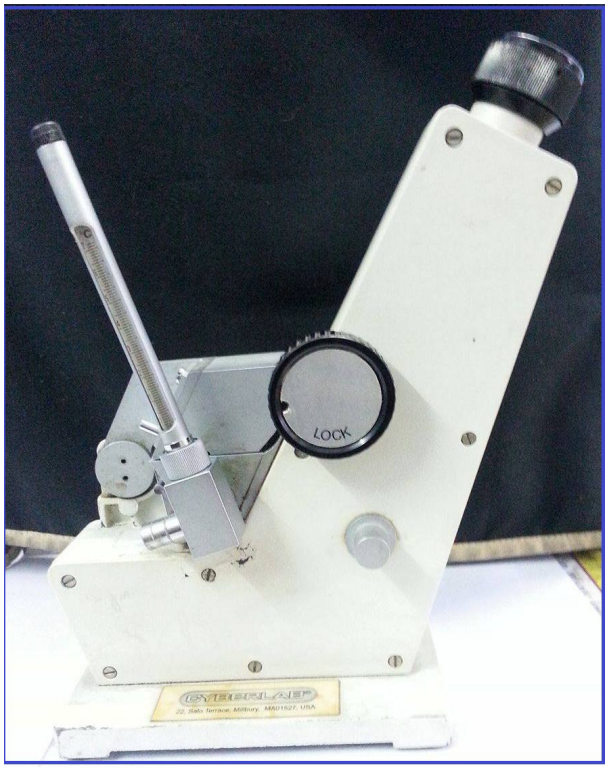

Fig. 3.5. Abbe Refractometer (Cyberlab, MA01527, USA).

3.2.5. Spectrophotometric measurements

Absorption spectra of food additives and drugs in different aqueous solvent systems were recorded on a Jasco V-530 double beam UV-VIS spectrophotometer at 298.15 K. Figure 3.6 shows the UV-VIS Spectrophotometer used. It was coupled with a thermostatic arrangement and maintained at 298.15 K. A quartz cell of 1 cm path length was used for the spectral measurements.

During spectrophotometric measurements stock solution of a food additive or drug was prepared in the mixed aqueous solvent systems and 2.0 mL of it was taken in the

quartz cell and absorption was measured against a selected spectroscopic grade reference solvent. Then solution of co-solute (of fixed concentration) in a mixed solvent or in the reference solvent was added in a stepwise fashion through a pre-calibrated Hamilton syringe. The absorbance of the solution was measured at each step within 30 seconds after mixing.

Fig. 3.6. Jasco V-530 double beam UV-VIS Spectrophotometer.

3.2.6. Ultrasonic Velocity Measurements

Speeds of sound were measured by multifrequency ultrasonic interferometer (F-05, Mittal Enterprises, New Delhi, India) working at 2MHz. Fig. 3.7 shows the multifrequency ultrasonic interferometer used. Its calibration was carried out with doubly distilled degassed water and purified methanol at (298.15±0.01) K by circulated thermostatic water around a jacketed cell (2MHz) filled it with the experimental liquid with circulating pump. The uncertainty of sound velocity was ±0.1 $m.s^{-1}$.

The principle used in the measurement of the sound velocity (u) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (γ) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal.

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 crystal and the anode

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

$$\text{Velocity } (u) = \text{Wave Length } (\lambda) \times \text{Frequency } (\gamma) \qquad (1)$$

Adiabatic Compressibility (β_s) can then be calculated by the following formula [9]:

$$\beta_s = \frac{1}{u^2 \rho} \qquad (2)$$

where ρ is the density of the experimental liquid.

Fig. 3.7. Multifrequency ultrasonic interferometer.

3.2.7. pH Measurements

A Systronics digital pH meter was used to measure the pH's of the solutions. Before the measurements, the instrument was calibrated at pH = 4.00. Fig. 3.8 shows the Systronics digital pH meter used.

Fig. 3.7. Systronics digital pH meter.

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