EXPERIMENTAL
3. EXPERIMENTAL

This chapter deals with the specifications of the chemicals and methods of their purification. It also includes the description of experimental techniques used for measuring conductance, density, viscosity and ultrasonic velocity of microemulsions.

3.1 Chemicals and their sources

Chemicals used in the present study are listed in table 1 along with their sources and grades.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tween 20</td>
<td>Hi Media Laboratories Pvt. Ltd.</td>
<td>pure</td>
</tr>
<tr>
<td>Tween 80</td>
<td>Sigma</td>
<td>pure</td>
</tr>
<tr>
<td>Span 20</td>
<td>Fluka AG Buchs</td>
<td>pure</td>
</tr>
<tr>
<td>Span 40</td>
<td>Koch Light Laboratories</td>
<td>pure</td>
</tr>
<tr>
<td>Span 60</td>
<td>Koch Light Laboratories</td>
<td>pure</td>
</tr>
<tr>
<td>Span 80</td>
<td>Koch Light Laboratories</td>
<td>pure</td>
</tr>
<tr>
<td>Benzene</td>
<td>Sisco Research Laboratory</td>
<td>HPLC (99.8%)</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>Merck Schuchardt</td>
<td>pure (99.0%)</td>
</tr>
<tr>
<td>Toluenene</td>
<td>E. Merck (India)</td>
<td>pure (99.0%)</td>
</tr>
<tr>
<td>O-Xylene</td>
<td>Fluka AG Buchs</td>
<td>pure (99.0%)</td>
</tr>
<tr>
<td>n-Proporol</td>
<td>Sarabhai M. Chemicals</td>
<td>pure (99.5%)</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>Sisco Research Lab.</td>
<td>pure (98.0%)</td>
</tr>
<tr>
<td>n-Pentanol</td>
<td>Fluka AG Buchs</td>
<td>pure&gt;(98.0%)</td>
</tr>
<tr>
<td>n-Hexanol</td>
<td>Fluka AG Buchs</td>
<td>pure&gt;(98.0%)</td>
</tr>
<tr>
<td>n-Heptanol</td>
<td>Fluka AG Buchs</td>
<td>pure&gt;(99.0%)</td>
</tr>
<tr>
<td>n-Octanol</td>
<td>Fluka AG Buchs</td>
<td>pure&gt;(99.0%)</td>
</tr>
<tr>
<td>n-Decanol</td>
<td>Fluka AG Buchs</td>
<td>pure&gt;(99.0%)</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>Glaxo India ltd.</td>
<td>A.R (99.9%)</td>
</tr>
</tbody>
</table>

3.1.1 Purification of chemicals

Propanol and butanol were dried over calcium sulphate and fractionally distilled. Pentanol, hexanol and heptanol were dried over calcium sulphate and fractionally distilled under reduced pressure.
pressure. Octanol and decanol were dried overnight over calcium sulphate and fractionally distilled under vacuum. The middle fraction at constant temperature was collected. Rest of the chemicals were used without further purification.

3.2 Conductivity measurement

Digital conductivity meter [Model NDC (732)] from Naina Electronics was used for making conductivity measurements. It consists of a wheatstone bridge circuit and a direct reading display. The solution under investigation was taken in a container (figure 2) and a conductivity cell (cell constant = 11.7 m\(^{-1}\)) was dipped into it. The frequency of the bridge is normally 50 Hz, suitable for high resistivity electrolytes. For highly conductive solutions it is 1000 Hz. This is selectable with a switch. The special features of the instrument are:

- High accuracy i.e. ± 3% of the displayed scale reading.
- Automatic decimal placement
- Direct measurement
- Large scale integration technique
- Inbuilt independent oscillator.

3.2.1 Principle of measurement

Determination of conductivity involves measuring the resistance of a column of solution. To avoid the effect of polarisation an alternating current of 1 KHz frequency is used.

A suitable amplitude of 1 KHz sinusoidal signal is applied on to the cell in solution under test. The resultant AC current is rectified and fed to the digital panel meter after suitable amplification and signal processing to make it possible for taking conductivity measurements at different temperatures with
Fig. 2. Double walled conductivity cell.
conductivity cells of different cell constants. The measurement of electrical conductivity is one of the key methods for the study of microemulsions.

3.3 Density measurement

Densities of pure components and the various microemulsions have been determined by making use of an Austrian precision densimeter Anton Paar (Model DMA 60). A brief description of the instrument is given below.

3.3.1 Principle of measurement

The measuring principle of the instrument is based on the change of natural frequency of a hollow oscillator when it is filled with different liquids. The mass and thus the density of sample changes the natural frequency of the oscillator due to its gross mass change on introduction of a liquid. Since the direction of oscillations of the U tube is perpendicular to its plane, the frequency of the oscillator is only influenced by that fraction of the volume of fluid which is actually in the vibrating part of sample tube. It is hence essential to ensure that the sample tube is completely filled. This makes separate volume measurements unnecessary since the volume inside the sample tube is always the same.

For density calculations, we may consider an equivalent system represented by a hollow body of mass \( M \), which is suspended on a spring with an elasticity constant, \( 'C' \), its volume \( 'V' \) filled with a sample of density \( \rho' \). The natural frequency of this will be
\[ f = \frac{1}{2\pi} \sqrt{\frac{C}{M + V}} \]  \hspace{1cm} (4)

therefore, the period

\[ T = \frac{1}{f} \]  \hspace{1cm} (5)

\[ = \frac{2\pi}{\sqrt{(M + fV / C)}} \]  \hspace{1cm} (6)

\[ T^2 = 4\pi^2 (M + fV / C) \]  \hspace{1cm} (7)

\[ = (4\pi^2 M / C) + (4\pi^2 fV / C) \]  \hspace{1cm} (8)

\[ = B + A\phi \]  \hspace{1cm} (9)

Since \( A \) and \( B \) contain the volume \( V \), spring constant \( C \) and mass \( M \), these may be regarded as apparatus constant. The density \( \rho \) of unknown sample is related to square of the time period of the oscillator as

\[ \rho = \frac{T^2 - B}{A} \]  \hspace{1cm} (10)

for the difference of densities of two samples,

\[ \rho_1 - \rho_2 = \frac{1}{A} (T_1^2 - T_2^2) \]  \hspace{1cm} (11)

\[ = K (T_1^2 - T_2^2) \]  \hspace{1cm} (12)

The latter relationship is used to determine constant \( A \). Once \( A \) is known \( B \) can be determined from equation (10) provided \( \rho \) is known.
3.3.2 Description

The instrument consists of two distinct units viz.

1) Paar digital densimeter, Model DMA 60
2) An external measuring cell, DMA 602

1) DMA 60 densimeter consists of

- an 8 decimal place digital period meter with selectable resolution.
- as electronically temperature controlled quartz crystal time base of higher stability.
- a drift free frequency multiplier circuit according to principle of phase locked loop.
- continuous analog output of either the last two or three decimal digits of period value T.
- eight data storage with a control logic for a digital printer.
- as well as necessary system for the control of measurement and power supply.

Density is measured by measuring time period of oscillation of a vibrating U tube which is either filled with sample or through which the sample is continuously flowing. This U tube is located in sample cell. Frequency signals from the cell are transmitted in to the DMA 60 via connectors marked 'cell 1' and 'cell 2'. The signals after passing through an optical oscillator and noise filter are fed into the periodmeter. The built in time base gives clock pulse every $10^{-5}$ sec. The period meter measures the time for the number of preselected oscillator periods by counting the number of clock pulses for the number of oscillations selected by the "period select switch". In this way it is possible to get time period 'T' with high resolution within very short time.
2) DMA 602: It is standard version of a remote measuring cell. The cell is contained in its own separate housing, complete with oscillator counter mass and thermostat connectors. The sample tube made out of borosilicate glass (Duran 50) is fused into a double walled glass cylinder. The space between the U-shaped sample tube and the inner wall of cylinder is filled with a gas of high thermal conductivity which facilitates a rapid temperature equilibrium of the sample inside the oscillator tube with the thermostat liquid flowing through the double walled cylinder around the U tube.

The rest of the instrument consists of an electronic excitation system for the oscillator and the electronic which assure an interference free transmission of the period signal to DMA 60, and a built in air pump to dry the sample tube.

### 3.3.3 Method of density measurements

Before carrying out measurements of an unknown sample the instrument is calibrated with a calibrating liquid of known density.

When the illumination is off, the readings with the empty sample tube corresponds to T period for air. The light is switched on and the sample tube is filled with the calibrating liquid with a syringe. The filling should be carried out by moving slowly the syringe holder to make sure that the liquid properly wets the walls of the sample tube. The meniscus of liquid should be concave to avoid the trapping of micro air bubbles and hence to obtain stable readings. The sample tube is completely filled when the liquid meniscus has passed the upper
enlarged portion of the sample tube. The upper opening of the sample tube is closed with a teflon stopper. The illumination is turned off and the time period is noted. The liquid is sucked back into the syringe and the sample tube is flushed with alcohol or acetone. The nose from the built in air pump is now connected to the upper opening of the sample tube and the air is allowed to flow through it. After the pump is turned off, the resulting 'T' value for air should coincide with the T value for air noted earlier to ensure that the sample tube was dry. Instrument constants A and B are calculated as,

$$A = \frac{T^2_{\text{benzene}} - T^2_{\text{air}}}{\varphi_{\text{benzene}} - \varphi_{\text{air}}}$$  \hspace{1cm} (13)

$$B = T^2_{\text{air}} - A \times \varphi_{\text{air}}$$  \hspace{1cm} (14)

For an unknown liquid, density is given by equation

$$\rho = \frac{(T^2 - B)}{A}$$

For a liquid or mixture of unknown density the same operation as outlined above was repeated and T period was noted, hence \( \rho \) was calculated by using equation 10. The estimated error in density is \( \pm 1 \times 10^{-5} \) g cm\(^{-3} \).

3.4 Ultrasonic velocity measurements

Ultrasonic velocity measurements stand as one of the primary techniques for study of properties of matter such as mechanical, electromagnetic and particle interactions. The propagation of
high frequency stress waves is determined by the measurement of velocity and attenuation of ultrasonic waves as a function of any environmental variable such as temperature, pressure etc.

Two standard techniques measuring ultrasonic attenuation and velocity are -

1. Continuous wave method (CW method)
2. Pulse echo method (PE method)

The CW method is generally adopted in KHz regions. For low loss specimen, it is possible to achieve high sensitivities with this method. The CW method suffers from -

- The presence of extra complicating modes of vibrations
- Boundary effects
- The need for larger energy dissipation and subsequent heating of the system.
- Lack of good accuracy and precision.

The pulse echo method overcomes most of the limitations of the CW method and is, therefore, widely used.

In the commonly used pulse echo technique on ultrasonic frequency burst is introduced into the sample through a piezoelectric transducer bonded to the specimen. The ultrasonic pulse travels through the sample and an echo is registered each time it returns to the transducer. The amplitude of successive echoes decrease experimentally due to attenuation in the sample. In general the amplitudes are related by

$$A_2 = A_1 e^{-xd}$$  \hspace{1cm} (15)

where

$A_1$ and $A_2$ = amplitudes of echoes
$d$ = distance traveled by ultrasonic move between registering the two echoes.
$x$ = attenuation Co-efficient.
The above equation yields

\[ x = \frac{1}{d} (\ln A_1 - \ln A_2) \quad (16) \]

Ratio of two amplitudes is generally expressed in decibels or nepera. Thus

\[ x = \frac{2.303}{d \log_{10}(A_1/A_2)} \text{ db/unit length (or)} \quad (17) \]
\[ x = \frac{1}{d \log_{10}(A_1/A_2)} \text{ nepera/unit length} \quad (18) \]

For measuring the velocity of the ultrasonic wave, time elapsed between registering \( A_1 \) and \( A_2 \) (\( T \)) is to be measured accurately. Then velocity (\( u \)) in the sample is given by

\[ u = \frac{d}{T} \quad (19) \]

Oscilloscope is the simplest equipment by which one can measure both attenuation and velocity. Obviously, simpler the equipment used, cruder will be the measurement. Some of the widely used methods to measure velocity to high resolution and accuracy are

1. Sing around system
2. Pulse-echo-overlap method
3. Pulse superposition technique.

Pulse-echo-overlap technique is very powerful technique because it is possible to make absolute as well as relative measurements with high degree of accuracy. As both the echoes, involved in the measurement in PEO method, pass through the same electronic system, any change in transit time of various devices employed will introduce zero error. It is also insensitive to system gain changes including attenuation changes in the sample.
The absolute accuracy of velocity measurement using this technique is as high as 2 parts in $10^4$.

The other advantages of PEO method over the other-method are:

1) It may operate either with the transducer bonded directly to specimen or with buffer rod interposed between the transducer and specimen.

2) It may be operated with broad band pulses as well as rf bursts.

### 3.4.1 Principle of measurement

The principle of measurements is to make two signals of interest overlap on the oscilloscope by driving the X-axis with a frequency whose period is the travel time between the signals of interest. Then one signal appears on one sweep of the oscilloscope and the other signal appears on the next sweep. The X-axis frequency is supplied by the CW oscillator. For jitter-free overlap, the signals of interest must be synchronised with the phase of the CW voltage. This condition is achieved by generating the repetition rate of the input pulse from the phase of the CW voltage by a frequency divider. Division by a large number (e.g. 1000) allows the echoes from one pulse to be attenuated before the next pulse is applied. The output of the frequency divider is a trigger signal, synchronous with the phase of the CW voltage. The trigger signal triggers the main pulser, which pulses the transducer. A diode limiter circuit keeps the input pulse from overloading the amplifier. The main pulser also triggers two intensifying pulses, which are applied to Z-axis of the scope, to intensify the trace. This feature is necessary to
distinguish the two signals of interest from the rest of the echoes in the trace.

### 3.4.2 Method of measurement

To make measurements, one first sets the oscilloscope on the triggered mode of operation. The delays and widths of intensity pulse are then adjusted to cover the signals of interest. The frequency of CW oscilloscope is set at approximately the reciprocal of travel time between signals of interest. The oscilloscope is then switched to drive X-axis mode of operation. The intensity of cathode ray tube is turned down so that only the intensified peaks are visible, and the main pulser delay is adjusted so that these signals are in the center of the screen. Then CW oscillator frequency is adjusted, so that the two signals overlap as shown in figure 3.

In the pulse echo overlap method, an overlap will appear not only when time between signals of interest is equal to reciprocal of CW oscillator frequency but also for any integer multiple 'm' of CW oscillator. This means that the two echoes will appear on \( m^{th} \) and \( 2m^{th} \) sweeps of oscilloscope instead of on first and second after the occurrence of input pulse.

### 3.5 Viscosity measurements

These were carried out using suspended level dilution ubbelohde viscometer (figure 4). For maintaining accuracy and reproducibility of results, the viscometer was cleaned with warm chromic acid and washed several times with distilled water. Finally, the viscometer was rinsed with alcohol followed by
Fig. 3. Overlap achieved by echoes.
Fig. 4.  Modified form of Ubbelohde viscometer.
acetone and was dried under vacuum. The initial microemulsion sample was prepared in the viscometer itself. The viscometer containing the microemulsion was placed in a water bath maintained at 303.15 K. The time of flow was measured accurately using electronic digital display stopwatch up to ± 0.01 sec. The measurements were repeated to get the concordant readings. Further, dilutions were made to cover a wide range of water concentrations. The precision in measured viscosity values is ± 0.3 %.

3.5.1 Kinetic energy correction

Poisuille [61] derived the following relation for flow of a liquid through a capillary tube.

\[ \eta = \frac{\pi Pr^4 t}{8VL} \]  

(20)

where
\( \eta \) = coefficient of viscosity in Poise.
\( P \) = driving pressure or constant vertical pressure in dyne/cm\(^2\) for maintaining a uniform rate of flow.
\( r \) = radius of the capillary in cm.
\( V \) = Volume of the liquid in cm\(^3\) which flows through the capillary.
\( t \) = time of flow in seconds
\( l \) = length of the capillary in cm.

This equation holds accurately for streamlined flow but not for turbulent flow which sets in at high velocity. It does not include kinetic energy correction terms. If the driving pressure is due to force of gravity, then

\[ P = h \rho g \]  

(21)

where
\( h \) = height of the driving head
\( \rho \) = density of the liquid
\( g \) = Acceleration due to gravity.
The equation then becomes

$$\eta = \frac{r^4 \delta g t}{8VL}$$  \hspace{1cm} (22)

The exact equation for the laminar flow of a liquid through a cylindrical tube may be written as

$$\eta = \frac{r^4 \delta g t}{8V(L+nr)}$$  \hspace{1cm} (23)

where $\eta$ is a coefficient associated with flow at the end of the capillary.

More accurately, stream-lined flow through a tube or capillary is expressed by Bingham [62] and Reimen [63] as

$$\eta = \frac{r^4 \delta g t}{8V(L+nr)} - \frac{m\delta V}{8\pi(L+nr)t}$$  \hspace{1cm} (24)

where $m$ is another coefficient associated with flow at the end of the capillary.

The first term incorporates the law determined experimentally by Poisuelle and second term arises from the work done in accelerating and decelerating the fluids at the end of a capillary. Martin [64] has used the formula in a simplified form as

$$\eta = A \sigma t - B \sigma / t$$  \hspace{1cm} (25)

or

$$\eta / \sigma = A \sigma t - B / t$$  \hspace{1cm} (26)

where
\[
A = \frac{\pi r^4 h g}{8V(L+nr)} = \text{Constant} \quad (27)
\]
\[
B = \frac{mV}{8\pi (L+nr)} = \text{Constant} \quad (28)
\]

where A and B are viscometer constants and \(\eta/\rho\) is the kinematic viscosity.

The viscometer constants A and B were determined from the measured efflux times and the densities of two or more liquids of known viscosity. Martin’s equation (25) has been employed in the present investigation for the determination of viscosity of the microemulsions.

3.6 Preparation of microemulsion

The preparation of microemulsion is not an easy task. One has to prepare a large number of formulations of different compositions by hit and trial method to get the proper ratio of all the components i.e. oil, surfactants and cosurfactant. A good microemulsion is one which has as little as possible amount of alcohol and has the capacity to solubilize a large amount of water before turning turbid again.

A large number of w/o microemulsions were formulated containing Tween 20/Tween 80/Span 20/Span 40/Span 60/Span 80 as surfactant, benzene/toluene/ethyl benzene/o-xylene as oils, propanol/butanol/pentanol/hexanol/heptanol/octanol/decanol as cosurfactant with triply distilled water/1M NaCl/2M NaCl as aqueous phase. The emulsifier (surfactant and alkanol) was mixed with the oil in the proportion (by weight) 0.6-0.7 surfactant:
0.07–1.3 alkanol : 0.2–0.23 oil. Water/1M NaCl/2M NaCl was then added to give the desired final composition i.e. different volume fractions of water $\phi$. Usually the mixture was stirred to hasten the formation of the microemulsions. However, these systems form spontaneously. The ratio of number of moles of alcohol to the number of moles of surfactant ($n_a/n_s$) was kept as 2 (constant).

The measured values of conductance ($\sigma$), viscosity ($\eta$), ultrasonic velocity ($u$) and density ($\rho$) for all these systems are listed in Tables 2–31 (appendix).