**Materials**

Purified and redistilled acetone and toluene (Qualigens, ExcelaR) were used in the calibration of dilatometer and viscometer. Potassium chloride used in the cell constant determination was a Glaxo (AR) product. Sodium bromide used as additive in the surfactant solutions was a Qualigens product. The surfactants employed in the study were Dodecylethyldimethylammonium Bromide (Sigma, USA) and Cetyldimethylethylammonium Bromide (Sigma, USA). Cetyldimethylethylammonium Bromide used contains 85% Cetyldimethylethylammonium Bromide and 15% Stearyldimethylethylammonium Bromide. Therefore, its average molecular weight was used in the calculation to prepare a stock solution. All solutions were prepared in triply distilled water of specific conductance $0.5 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at 25°C.

**Methods**

**Purification**

Acetone [104]: Acetone was dried with anhydrous calcium chloride for twenty four hours and filtered. It was refluxed with sodium carbonate and distilled twice. Precautions to avoid moisture were taken and purity was checked by measuring the refractive index which was fairly reproducible.
Toluene[104]: Toluene was shaken repeatedly with about 15% of its volume of concentrated sulphuric acid in a separating funnel to remove any methylthiopene till the acid layer remained colourless. It was then washed with 10% sodium carbonate solution and finally with water. The sample was dried with calcium chloride and filtered. The filtrate was fractionally distilled and the fraction at 110 - 111°C collected. Sodium wire was introduced into distilled liquid before closing the bottle with a stopper.

Temperature Control

For density, viscosity and conductometric measurements a thermostatic water bath was used to maintain the temperature constant within ±0.05°C. The bath consisted of a Remi Stirrer, a check thermometer (TGL - 4850, NAV = 0.03A) and a check thermometer (un = 250 V, GDR). The check thermometer was NBS calibrated. Temperature was controlled with the help of an electronic relay (Jumo - Type NT 15.0, 220 V, 15 A, GDR) working in combination with the contact thermometer and an immersion rod (220 V, 1000 W) connected through a dimmerstat to the power supply.

Calibration of Dilatometer [105, 106]

A dilatometer with a bulb capacity of 23 cm³ and a stem of length 12 cm and internal diameter 2 mm with a ground glass stopper was used. The graduations on the stem with a volumetric distance of about 0.2cm³ were calibrated with triple distilled water of known density [107]. The dilatometer was thoroughly rinsed with chromic acid, washed with water and dried in an oven. After cooling in a desiccator it was weighed on a digital balance (Anamed, 0.1mg) and filled with water slightly above the first mark on the stem. The bore above the meniscus was dried and the dilatometer weighed again to find the mass of water.
The filled dilatometer was immersed in the water bath and the temperature of the bath raised slowly till the meniscus touched the next mark on the stem. Temperature on each mark was noted only after the meniscus remained stationary for at least 15 minutes. The known densities \( \rho \), of water between 20° to 50°C were least-squares fitted to the equation.

\[
\rho = a + b.T + c.T^2 \tag{2.1}
\]

with respect to temperature \( T \) to get the best fit parameters \( a, b \) and \( c \). Eq. (2.1) gave a better fit for water densities than the linear equation. The parameters \( a, b \) and \( c \) were used to calculate density at the recorded temperatures and hence the volume \( V \) corresponding each mark on the stem was obtained from the equation \( V = m/\rho \), knowing the mass \( m \) of water. Altogether six marks were calibrated.

The procedure was repeated again with water and then with toluene. The fitting equation in case of toluene was

\[
\rho = a + bT \tag{2.2}
\]

as density of toluene is known to vary linearly with temperature. This provided the necessary cross check for the calibrated volumes on the dilatometer.

The accuracy of the calibration was reconfirmed by determining the densities of toluene and acetone at various temperatures and comparing them with the reported [107,108] values. The standard deviation of calculated densities from the reported values in case of toluene was \( \pm 4 \times 10^{-5} \).
The cannon Ubbelohde type suspended level viscometer consisted of three parallel arms, a receiving arm, a measuring arm and an auxiliary arm. The measuring arm consisted of a capillary of length 7cm with a bulb of about 15cm³ capacity at the bottom and 6cm³ at the top above which there is an auxiliary bulb of about 1.5cm³ in volume. The marks for measuring the flow of a constant volume of liquid were at the top and bottom of the upper bulb. The bulb at the bottom of the capillary was connected to the auxiliary arm and to the receiving arm which carried another bulb of about the same capacity.

The advantage of the suspended level viscometer is that it minimizes the back pressure due to the liquid column as the liquid flows freely under its own weight.

The thoroughly cleaned, dried and washed viscometer was filled with sufficient volume of distilled water to fill the auxiliary bulb, the upper bulb, the bottom bulb and a part of the receiving bulb. It was then clamped in the constant temperature bath with the auxiliary bulb about 1cm below the water level in the bath. The bath was maintained at the required temperature for half an hour for the viscometer contents to attain thermal equilibrium. After gently and carefully sucking water through the capillary upto the top of the auxiliary bulb and keeping it standing for about 3 minutes it was allowed to flow freely. The time of flow between the two marks was recorded with a stop watch (Racer, Swiss) with an accuracy of 0.1 s. At least four concordant readings were taken at each temperature.

The equation \[ \eta = b' \cdot \rho \cdot t - c' \cdot \rho / t \] based on Poiseulle's law was used to find the viscometer constants \( b' \) and \( c' \). \( \eta \) and \( t \) represent the viscosity and time of fall respectively. The second term in the equation is a
measure of the back pressure due to the column of liquid in the capillary. Although its magnitude is small, it is included for more accurate results. The constants $b'$ and $c'$ were calculated by simultaneous solution of Eq. (2.3) after putting in the known values of viscosity and density of water [107] at 30°C and 40°C and the recorded times of fall at these temperatures. The values of $b'$ and $c'$ thus obtained were used to calculate the viscosity of water at 25°C. The deviation of calculated viscosity from the reported value was found to be ±0.15%.

The calibration of the viscometer was cross-checked by determining the viscosity of acetone and toluene at 25°C and the values compared fairly well with the reported [113] ones. Reproducibility of the results was ±4×10⁻⁴ mN s m⁻². The values of viscometer constants $b'$ and $c'$ were 3.533×10⁻³ and 5.667 respectively.

**Measurement of Density**

Densities of solutions of DEDMAB and CDMEAB in water as well as in aqueous NaBr were determined with the calibrated dilatometer. The dilatometer was filled up to a level slightly below the first calibrated mark and after weighing was immersed in the constant temperature bath. Temperature was increased slowly till the meniscus coincided with the mark. When the meniscus remained stationary at the mark for nearly 15 minutes the temperature was recorded. A similar procedure was followed for all the subsequent marks on the stem. The densities obtained by dividing the mass of the filled-in solution with the volume corresponding to each mark were least-squares fitted to the recorded temperatures to get the fitting parameters of the best fit line. It was found that solution densities fitted better to the linear equation (Eq. (2.2)) than to the quadratic equation (Eq. (2.1)). The best
fit parameters a and b were utilized to compute the densities of solutions at the required temperatures.

**Measurement of Viscosity**

The viscosity of a solution of given concentration was determined with the calibrated viscometer. The viscometer was cleaned, dried and filled with sufficient volume of solution and clamped in the thermostatic bath. After maintaining the bath at the required temperature for half an hour the flow time of solution was noted for a minimum of 4 concordant readings. Measurements were made between 20° to 50°C at 5° intervals. Viscosities were then calculated with Eq. (2.3).

**Errors and Their Elimination**

i. The error due to thermal expansion of glass of the viscometer and the dilatometer was compensated for in the calibration.

ii. No correction was made in the suspended level for the difference in thermal expansion between the calibrating liquid and test solution.

iii. The flow undergoes a sudden fluctuation upon entering and leaving the capillary (turbulent flow). Viscosity of flow is less near the ends than inside the capillary. The effect may be considered as equivalent to an increase in effective length of the capillary. However, this correction becomes insignificant as the ratio of the length to the radius of the capillary becomes large.

iv. The drainage error arises from the fact that a thin layer of liquid remains adhering to the wall of the reservoir. But this error is very small for organic liquids and the correction applies both to the test solution and the calibrating liquid and becomes insignificant when only relative viscosities are measured.

v. A major source of error would be due to the back pressure of liquid in the capillary. Hence, this was eliminated by including the term \(-c'\cdot\rho/\mu\) in the poiseulles equation which also takes care of the end effects.
**Measurement of Conductivity**

The dip-type conductivity cell (Elico, CC-03) was calibrated with aqueous KCl solutions using molar conductivity data reported by Jones and Bradshaw [114]. The cell constant was found to be 0.695 cm\(^{-1}\). For determination of conductivity the cell was dipped into the test solution contained in a boiling tube of 50 cm\(^3\) capacity which was immersed in the constant temperature bath. The cell was connected to a digital RLC meter (GR.1695, USA) having an accuracy of ±0.20%. The cell contents were allowed to reach thermal equilibrium with the bath to within ±0.05°C at the required temperature for half an hour after which resistance of the solution was recorded. Thermal stability was indicated by constancy of the reading. Resistances were measured at 5° intervals. The conductivities were computed from the corresponding resistances. The cell was thoroughly washed with water and dried before putting in the test solution. Reproducibility of the data was ±0.35%.

**Measurement of Sound Velocity**

The velocity of ultrasound waves in various solutions was determined by an Ultrasonic Interferometer (Mittal - M81). The instrument consists of a multifrequency generator and a measuring cell. The generator is designed to excite a quartz plate at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the solution placed in the cell. A micro-ammeter to observe the change in the current and two knobs for adjusting the current sensitivity are provided on the panel of the instrument.

The measuring cell is specially designed and double walled for maintaining the temperature of the experimental solution constant. The quartz plate is fixed at the bottom of the square base in which the cell is fitted and is connected to the generator through a flexible
co-axial cable. A fine micrometer screw provided at the top of the cell can raise or lower a
disc shaped reflector plate by a known distance through the solution in the cell.

Waves of desired frequency produced at the bottom of the cell after travelling
through the solution are reflected back by the reflector plate. If the distance traversed by the
waves before reflection in the solution is equal to an integral multiple of half wavelengths,
the current registered by the instrument is maximum. The displacement of the reflector plate
as recorded by the micrometer for twenty such maxima was measured and the average
displacement per maximum was calculated. This gives the half wavelength of sound waves
travelling in the solution. If \( d \) be the displacement for 20 maxima, the wavelength of
ultrasonic waves is given by

\[
\frac{\lambda}{2} = \frac{d}{20}
\]

or \( \lambda = \frac{d}{10} \) (2.4)

In actual practice the average of at least fifteen such readings was used to determine
the wavelength. Knowing the frequency \( \nu \) of the waves, their velocity in the solution could
be calculated as

\[
U = \lambda \times \nu
\]

(2.5)

**Measurement**

About 9ml of the test solutions was taken in the cell clamped in its base. The base
was connected to the instrument through the cable. Water at a fixed temperature (±0.05°C)
from a highly efficient thermostat (MLW, U10, Germany) was circulated through the space
between the double walls of the cell. Readings were taken only after sufficient time (~1 hour) was allowed for the cell contents to acquire the set temperature.

Measurements were made at a frequency of 4MHz in the temperature range 25 to 50°C at 5° intervals. Accuracy of the results was checked by comparing the measured velocity of sound with the reported value [115]. The precision of the measurement was 0.1 ms⁻¹.