

CHAPTER-II

EXPERIMENTAL SECTION

(Materials and Methods)

CHEMICALS

The surfactant lithium dodecylsulfate was from E. Merck, Germany and was used as received.

All the tetraalkylammonium salts were of purum or puriss grade (Fluka, Switzerland). These were purified as described in the literature¹⁻³. Generally these salts were purified by recrystallization. Higher tetraalkyl homologues were recrystallized twice to ensure the highest purity. The recrystallized salts were dried in vacuum and stored in a glass bottle in darkened dessicator over fused CaCl_2 .

Tetramethylammonium bromide (Me_4NBr) was recrystallized from a mixture of methanol and ethanol (1:1) and dried at 363 K for 24 hours.

Tetraethylammonium bromide (Et_4NBr) was recrystallized from methanol and dried at 363 K for 24 hours.

Tetrapropylammonium bromide (Pr_4NBr) was dissolved in a minimum volume of methanol, reprecipitated from dry ether and dried at 363 K for 48 hours.

Tetrabutylammonium bromide (Bu_4NBr) was dissolved in a minimum volume of acetone. Ether was added to the solution till the commencement of precipitation. The solution was then cooled and the resulting crystals were filtered. After a preliminary drying, the salts was finally ground in a mortar and dried at 333 K for 48 hours.

The nonionic amphiphiles polyoxyethylene (23) laurylether (Brij-35 or Bj-35) and polyoxyethylene (10) isoocetyl phenylether (Triton X-100 or TX-100) were from Sigma (USA) and were used without further purification.

The surfactant cetyltrimethylammonium bromide (CTAB) was purchased from Sigma (USA). Tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB) were of purum grade (Fluka, Switzerland) and were used as received.

SOLVENTS

Pure Solvents

Triply distilled water was used for preparing the experimental solutions. Water was first deionized and then distilled from an all glass distilling set using alkaline KMnO_4 solution. Doubly distilled water was then finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO_2 and other impurities. The triply distilled water had a specific conductance of less than $1.5 \times 10^{-6} \text{ Scm}^{-1}$.

Ethylene glycol (EG), G.R.E. Merck, was distilled twice in an all glass distillation set before use. The purified solvent had a density of $1.11000 \text{ g cm}^{-3}$, a coefficient of viscosity of 17.87324 cP and a specific conductance of ca $1.02 \times 10^{-6} \text{ Scm}^{-1}$ at 298.15 K ; these values are found to be in good agreement with the literature values^{4, 5}.

Methanol and acetone used were of A.R grade and great care was taken to ensure that ether was free from peroxide.

Mixed Solvents

The mixed solvents containing 0.10, 0.20, 0.30, 0.40, and 0.50 mass fractions of EG (w_1) were prepared accurately by mixing the requisite amounts of water and EG by weight. The dielectric constants (D), densities (ρ), viscosities (η) and specific conductances (κ) s of EG (1) + water (2) mixtures at 298.15 K are given in Table 1.

Preparation of Experimental Solutions

A stock solution for each surfactant and/or salt in water as well as in different mixed solvents was prepared by weight and the working solutions were obtained by weight dilution. The molar concentrations of the solution were calculated from molality and density values.

METHODS

Density Measurements

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at the experimental temperature with doubly distilled water. The precision of the density measurements was $\pm 3 \times 10^{-5}$ g cm⁻³. The measurements were made in an oil bath maintained within ± 0.005 K of the desired temperature by means of a mercury-in-glass thermoregulator and the absolute temperature was determined by a platinum resistance thermometer and Muller bridge⁶.

Viscosity Measurements

The kinematic viscosities were measured by means of a suspended-level Ubbelohde⁷ viscometer with a flow time of about 539 s for distilled water at 298.15 K. The time of efflux was measured with a stop watch capable of recording to ± 0.1 s. The viscometer was always kept in a vertical position in a water thermostat maintained within ± 0.01 K of the desired temperature. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.

Conductance Measurements

Conductance measurements were carried out on a Philips Pye-Unicam PW 9509 conductivity meter with an uncertainty of $\pm 0.1\%$. A 2000 Hz cycle was used. The cell constant (0.731 cm⁻¹) of the dip-type conductance cell was accurately determined using standard KCl solutions by the method of Lind *et. al.*⁸ The

measurements were made in an oil bath maintained within ± 0.005 K as described earlier under density measurements.

Compressibility Measurements

Ultrasonic velocity measurements were carried out in a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 5 MHz calibrated with water, methanol and benzene at each temperature. The temperature stability was maintained within ± 0.01 K by circulating thermostated water around the measuring cell by a circulating water bath. The maximum uncertainty of the sound velocity measurements in all cases was ± 0.03 %.

Surface tension Measurements

The surface tensions of the surfactant solutions were measured with a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The measured tensions were corrected according to the procedure of Harkins and Jordon⁷. The tensiometer was connected to a water-flow cryostat to maintain the temperature equilibration. Prior to each measurement, the ring was heated briefly by holding it above a Bunsen burner until glowing. Duplicate measurements were made to check the reproducibility. The uncertainty of measurements was within ± 1 mNm⁻¹.

Spectral Measurements

A UV-visible (240) Shimadzu (Japan) spectrophotometer operating in dual beam mode was employed for spectral measurements using matched pair of quartz cuvettes of pathlength 1 cm under thermostated condition (298.15 K). Spectral measurements were performed on the basis that TX-100 absorbs maximum at 276.5 nm and the absorbance (A) gets perturbed at the micellar point⁹. Here 3 mL of water was taken in a pair of cuvettes. Surfactant solution was then progressively added in the sample cell as required. Optical density at each stage of surfactant addition was measured after thorough mixing at the absorption maximum (276.5 nm) of TX-100.

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Table 1. Solvent Properties of EG (1) + Water (2) Mixtures at 298.15 K

$100w_1$	D	$\rho/\text{g cm}^{-3}$	η/cP	$\kappa/\text{S cm}^{-1}$
0	78.30	0.99707	0.89030	1.50×10^{-6}
10	75.65	1.00949	1.15197	6.32×10^{-6}
20	72.68	1.02245	1.46935	5.34×10^{-6}
30	69.77	1.03570	1.90253	5.11×10^{-6}
40	67.00	1.04943	2.56252	2.00×10^{-6}
50	63.93	1.06216	3.33176	1.42×10^{-6}
100	37.07	1.11000	17.87324	1.02×10^{-6}