CHAPTER-II

EXPERIMENTAL SECTION

(Materials and methods)

Chemicals

All salts (except tetrapentylammonium perchlorate and potassium, rubidium and cesium perchlorates) were of Fluka's purum or puriss grade.

Tetraalkylammonium salts were purified in the manner given in the literature[1,2]. Generally these salts were purified by recrystallization. Higher tetraalkyl homologues were recrystallized second time to ensure the highest purity. The crystallized salts were dried in vacuum and stored in glass bottles in darkened dessicator over fused $CaCl_2$.

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

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

Tetrabutylammonium bromide (Bu_4NBr) was taken 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 salt was finally ground in a morter and dried at 333K for 48 hours.

Tetrapentylammonium bromide (Pen_4NBr) was recrystallized from acetone + ether mixtures and dried in vacuo at 333K for 48 hours.

Tetrahexylammonium bromide (Hex_4NBr) and tetraheptylammonium bromide (Hep_4NBr) were washed with ether and dried in vacuo at room temperature for 48 hours.

Tetrapentylammonium perchlorate (Pen_4NClO_4) was prepared by adding slowly a hot aqueous solution of tetrapentylammonium bromide to a hot aqueous solution of sodium perchlorate ($NaClO_4$). All the tetraalkylammonium perchlorate salts were recrystallized twice from conductivity water and dried in vacuo at 343K for 24 hours.

Lithium perchlorate ($LiClO_4$) was recrystallized three times from conductivity water and then dried under vacuum for several days[3]. Sodium perchlorate ($NaClO_4$) was recrystallized several times from water + methanol mixtures and dried in vacuo at 423K for 96 hours. Other alkali metal perchlorates were prepared by precipitation by adding $NaClO_4$ to a solution of the corresponding chlorides in anhydrous methanol and and were recrystallized 8 to 10 times from a mixture of water + methanol, 1:1 by volume and dried in vacuum at 473K for several days[4].

Sodium tetraphenylborate ($NaBPh_4$) was recrystallized 3 times from acetone and then dried in vacuum at 353K for 72 hours.

Lithium tetrafluoroborate ($LiBF_4$) and lithium hexafluoroarsenate ($LiAsF_6$) were dried under vacuum at high temperatures for 48 hours and were used without further purification.

Solvents

2-Methoxyethanol (ME) (G.R.E. Merck) was distilled twice in an all glass distillation set before use. The purified solvent had a density of 0.96002 g cm^{-3}, a coefficient of viscosity of 1.5414 cP and a specific conductance of ca 1.01×10^{-6} Scm^{-1} at 25°C; these values are in good agreement with the literature values[5], which are 0.96024 gcm^{-3}, 1.60 cP and 1.09×10^{-6} Scm^{-1} (at 20°C) respectively.

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. The double 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 1×10^{-6} Scm^{-1}.

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 20, 40, 60 and 80 Wt% of ME were prepared accurately by mixing the requisite amounts of H_2O and ME by weight. Solvent properties of ME + H_2O mixtures at 25°C are given in Table 1.

Table 1 . Solvent properties of (ME + H_2O) mixtures at 25°C

Wt% of ME	ϵ	ρ / gcm^{-3}	η / cP	Sp. conductance / Scm^{-1}
0	78.32	0.99707	0.8903	1.01×10^{-6}
20	69.73	1.00240	1.5165	37.30×10^{-6}
40	57.41	1.00690	2.3654	20.00×10^{-6}
60	42.11	1.00233	2.8849	7.22×10^{-6}
80	26.53	0.98672	2.5751	3.84×10^{-6}
100	16.93	0.96002	1.5414	1.01×10^{-6}

Preparation of experimental solutions

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

Methods:

(a) Density measurements

The densities were measured with an Ostwald-Sprengal type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25, 35 and 45°C with doubly distilled water. The precision of the density measurements was $\pm$ 3 x 10^{-5} gcm^{-3}. The measurements were made in an oil bath maintained with an accuracy of $\pm$ 0.005°C 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 bridge[6].

(b) Viscosity measurement

The kinematic viscosities were measured by means of a suspended-level Ubbelohde[7] viscometer with a flow time of about 539s for distilled water at 25°C. The time of efflux was measured with a stop watch capable of recording $\pm$ 0.1 s. The viscometer was always kept in a vertical position in a water thermostat. The viscometer needed no correction for kinetic energy. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = Ct - K/t \qquad (1)$$

$$\eta = \nu\rho \qquad (2)$$

where t is the efflux time, ρ is the density and C and K are the characteristic constants of the viscometer. The values of the constants C and K, determined by using water and benzene as the calibrating liquids at 25, 35 and 45°C, were found to be 1.648×10^{-5} $cm^2 s^{-2}$ and -0.02331647 cm^2 respectively. The precision of the viscosity measurements was ± 0.05%. In all cases the experiments were performed at least in five replicates and the results were averaged.

Relative viscosities (η_r) were obtained using the equation (3):

$$\eta_r = \eta/\eta_o = \rho t / \rho_o t_o \qquad (3)$$

where η, η_o ; ρ, ρ_o and t, t_o are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic bath maintained with an accuracy of ± 0.01°C of the desired temperature[8]. A 60 W heating element and a toluene-mercury thermoregulator were used to maintain the temperature of the experimental thermostat which was placed in a hot-cum-cold thermostat. The temperature of the hot-cum-cold thermostat was preset at the desired temperature using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.

(c) Conductance measurements

Conductance measurements were carried out on a Philips Pye-Unicam PW 9509 conductivity meter with an accuracy of ± 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 . Conductivity cell was sealed to the side of 500 cm^3 conical flask closed by a ground glass cap fitted with a side arm through which dry and pure nitrogen was passed to prevent the admission of air into the cell when solvent or solution was added. The measurements were made in an oil bath maintained at 25 ± 0.005°C as described earlier under density measurements. All data were corrected with the specific conductance of the solvent.

(d) 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. The temperature stability was maintained at ± 0.01°C by circulating thermostated water around the measuring cell by a circulating water bath.

The principle used in the measurement of velocity (u) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (ν) 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 accoustic 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 wavelength ($\lambda/2$) or integral multiple of it, anode current again becomes maximum. From the knowledge of the wavelength (λ), the velocity (u) can be obtained by the relation:

$$\text{Velocity (u)} = \text{Wavelength } (\lambda) \times \text{Frequency } (\nu) \qquad (4)$$

Adiabatic compressibility (β) can then be calculated by the following formula:

$$\beta = 1 / u^2 \rho \qquad (5)$$

where ρ is the density of the experimental liquid.

The ultrasonic interferometer consists of the following two parts:

i) the high frequency generator and

ii) the measuring cell

The measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. The

cell is filled with the experimental liquid before switching on the generator. The ultrasonic waves move normal from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal.

The micrometer is slowly moved till the anode current on the high frequency generator shows a maximum. A number of maximum readings of anode current are passed on and their number (n) is counted. The total distance (r) thus moved by the micrometer gives the value of wave length (λ) with the following relation

$$r = n \times \lambda / 2 \qquad (6)$$

Once the wave length is known, the velocity can be calculated.

The maximum uncertainty of the sound velocity measurements in all cases was $\pm$ 0.03%.

R E F E R A N C E S

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