CHAPTER I I

Experimental Section
(Materials and Methods)

Chemicals

All salts were of Fluka's purum or puriss grade.

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

Tetraethylammonium bromice (Et_4NBr) was recrystallised from methanol and dried at 363 K 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 recrystallised 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.

Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepred by disolving sodim tetraphenylborate in distilled water (2% solution) and filtred to remove a small amount of insoluble impurities. To this an equivalent amount of tetrabutylammonium bromide in 2% aquous solution was slowly added. The bulky white precipitate thus obtained was wasted five times by decantation. After preliminary drying the product was recrystallised four times from 1 : 3 water-acetone mixture and finally dried for several days at 40^0C and 10^{-4} mm.Hg pressure (m.p 223-225^{0}C).

Solvents

Acetonotrile (E. Merck, 99%) was distilled with P_2O_5 and then with CaH_2 in an all–glass distillation set before use and the middle fraction collected. The purified solvent had a density of 0.77686 gm cm^{-3}, and a coefficient of viscosity of 0.345 mpas at 25^{0}C; these values are in good agreement with the literature values e.g. 0.776851 g cm^{-3} and 0.344 m.Pa.s respectively[3,4].

Methanol (E. Merck, India, Urasol grade) was dried over 3Å molecular sieres and distilled fractionally. Middle fraction was collected and redistilled. The purified solvent had a density of 0.78654 g.cm^{-3} and a coefficient of viscosity of 0.545 m.pa s at 298.15 K. these values are in good agreement with the literature values which are 0.7866 g.cm^{-3} and 0.5445 m.Pa.s, respectively.

The mixed solvents containing 0.0, 0.20, 0.40, 0.60 0.80 and 1.00 mole frction of acetonitrile were prepared accurately by mixing the requisite amounts of methanol and acetonitrile by weight. Solvent properties of methanol   + acetonitrile . mixtures at 298.15 K are given in Table 1.

Table 1.Solvent properties

mole fraction of acetonitrile	ε	ρ/gcm^{-3}	η/m.Pa.s
0.00	32.62	0.78654	0.545
0.20	33.58	0.78680	0.435
0.40	34.30	0.78465	0.373
0.60	34.92	0.78212	0.343
0.80	35.47	0.77952	0.334
1.00	35.95	0.77686	0.343

Preparation of experimental solutions

A stock solution for each salt in pure as well as in different mixed solvents was prepared by mass and the working solutions were obtained by mass 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 cm³ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 298.15, 308.15 and 318.15 K with doubly distilled water. The precision of the density measurements was $\pm 3 \times 10^{-5}$ gcm⁻³. The measurements were made in a water bath maintained with an accuracy of ± 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 bridge[6].

(b) Viscosity measurement

The kinematic viscosities were measured by means of a suspended-level Ubbelohde[6] viscometer with a flow time of about 539s for distilled water at 298.15 K. The time of efflux was measured with a stop watch capable of recording ± 0.1 s. The viscometer was always kept in a vertical position in a water thermostat.. The kinematic viscosity (v) and the absolute viscosity (η) are given by following equations :

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

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

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 acetonitrile and methanol benzene as the calibrating liquids at 298.15, 308.15 and 318.15 K were found to be 1.648×10^{-5} cm² s⁻² and -0.02331647 cm² respectively. The precision of the viscosity measurements was $\pm 0.02\%$. 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) :

$$\eta_r = \eta / \eta_0 = \rho t / \rho_0 t_0 \qquad (3)$$

where η, η_0 ; ρ, ρ_0 and t, t_0 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 K of the desired temperature[7]. 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 $\pm 0.01\%$. A 2000 Hz cycle was used. The cell constant (0.751 cm^{-1}) of the dip-type conductance cell was accurately determined using standard KCl solutions following the method of Lind and coworkers[8]. 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 298.15 ± 0.005 K 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 K by circulating thermostated water around the measuring cell by a circulating water bath.

The principle used in the measurements 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 :

Velocity (u) = Wavelength (λ) x Frequency (v) (4)

Isentropic compressibility (K_s) can then be calculated by the following formula :

$$K_s = 1 / (u^2 \rho)$$ (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 turning 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

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

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

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

References

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