

CHAPTER II

Experimental Section (Materials and Methods)

Chemicals

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

These are purified in the manner given in the literature¹⁻⁵. Generally these salts were purified by recrystallisation. Higher tetraalkyl homologous were recrystallised second time to ensure the highest purity. The crystallized salts dried in vacuum and stored in glass bottles in darkened dessicator over fused CaCl₂.

Tetraethylammonium bromide (Et₄NBr) was recrystallised from methanol and dried at 363 K for 24 hours.

Tetrapropylammonium bromide (Pr₄NBr) was taken in a minimum volume of methanol, reprecipitated from dry ether and dried at 363 K for 48 hours.

Tetrabutylammonium bromide (Bu₄NBr) 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 mortar and dried at 333K for 48 hours.

Tetrapentylammonium bromide (Pen₄NBr) was recrystallised from acetone and ether mixtures and dried in vacuo at 333K for 48 hours.

Tetraheptylammonium bromide (Hep₄NBr) was washed with ether and dried in vacuo at room temperature for 48 hours.

Tetrabutylammonium tetraphenylborate (Bu₄NBPh₄) was prepared by dissolving sodium tetraphenylborate in distilled water (2% solution) and filtered

to remove a small amount of insoluble impurities. To this an equivalent amount of tetrabutylammonium bromide in 2% aqueous solution was slowly added. The bulky white precipitate thus obtained was washed 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 313.15 K and 10^{-4} mm.Hg pressure (m.p.496.15-498.15 K).

Solvents

2-Ethoxyethanol (G. R. E. Merck) was dried with potassium carbonate and distilled twice in all glass distillation set immediately before use and the middle fraction was collected. The purified solution has a density (ρ_0) of $0.92497 \text{ g cm}^{-3}$ and a coefficient of viscosity (η_0) of 1.8277 mPa s at 298.15 K; these values are found to be in good agreement with the literature values^{9,10}.

The mixed solvents containing 25%, 50%, 75% of 2-ethoxyethanol by weight were prepared accurately by mixing 2-ethoxyethanol with triple distilled water. Solvent properties of 2-ethoxyethanol + water mixtures at 308.15, 313.05, 318.15 and 323.15 K are given in Table-1.

Table 1. Properties of 2-ethoxyethanol (1) + water (2) Mixtures with $w_1 = 0.25$, 0.50 and 0.75 at (308.15, 313.15, 318.15 and 323.15) K

T/K	$\rho_0 /(\text{g.cm}^3)$	$\eta_0 /(\text{mPa.s})$	ε
$w_1=0.25$			
308.15	1.00354	1.8430	60.13
313.15	1.00021	1.5293	58.70
318.15	0.99751	1.2738	57.37
323.15	0.99582	1.0923	56.11
$w_1=0.50$			
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.90
$w_1=0.75$			
308.15	0.95451	1.7002	27.93
313.15	0.95147	1.5293	27.29
318.15	0.94873	1.3498	26.68
323.15	0.94625	1.1901	26.10

Preparation of experimental Solutions

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

Methods

(a) Density measurements

The densities were measured with an Ostwald-Sprengal type pycknometer having a bulb volume of 25 cm^3 and an internal diameter of the capacity of about 1 mm. The pycknometer was calibrated at 308.15, 313.15, 318.15 and 323.15 K with double distilled water. The precision of the density measurement was $\pm 3 \times 10^{-5} \text{ gcm}^{-3}$. The measurements were made in a water bath maintained with an accuracy of $\pm 0.005 \text{ K}$ 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.

(b) Viscosity measurement

The kinematic viscosities were measured by means of a suspended-level Ubbelohde⁶ viscometer with a flow time about 539s for distilled water at 298.15 K. The time of efflux was measured with a stop watch capable of recording $\pm 0.1 \text{ s}$. The viscometer was always kept in a vertical position in water thermostat. The kinematic viscosity (v) and the absolute viscosity (η) are given by the following equations:

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

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

where t is the efflux time, ρ is the density and C and K are the characteristic constants of the viscometer. The values of constants C and K , determined by

using water, methanol, acetonitrile and 2-ethoxyethanol as the calibrating liquids at 308.15, 313.15, 318.15 and 323.15 K. were found to be $1.646 \times 10^{-5} \text{ cm}^2 \text{s}^{-2}$ and -0.02331647 cm^2 respectively. The precision of the viscosity measurements was $\pm 0.02\%$. In all the 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):

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

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 temperature⁷. 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 conductive 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 coworkers⁸. Conductivity cell was sealed to the side of 500cm^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 were 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.

References

- 1 B. E. Conway, R. E. Verral and J. E. Desnoyers, *Trans. Faraday Soc.*, **62**, 2738 (1966).
- 2 D.F. Evans, C. Zawoyski and R. L. Kay, *J. Phys. Chem.*, **69**, 3878 (1965).
- 3 J. Singh, T. Kaur, and D .S. Gill, *J. Chem. Soc, Faraday Trans.*, **90**, 579 (1994).
- 4 G. Moumouzias, D. K. Panopoulos and G. Ritzoulis, *J. Chem Eng. Data*, **6**, 20 (1991).
- 5 D. Dasgupta, S. Das and D. K. Hazra, *J. Chem. Soc., Faraday Trans*, **1**, **84**, 1057 (1988).
- 6 J. R.Suindell, J. R. Coe, Jr. and T. B. Godfray, *J.Res.Natd. Bur. Stand.*, **48**, 1 (1952).
- 7 S. K. Ghosh and D. K. Hazra, *Ind. J. Chem.*, **29A**, 656 (1990).
- 8 J. E. Lind, Jr., J. J. Zwolenik and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).
- 9 G. Douheret and A. Paul, *J. Chem. Eng. Data.*, **32**, 40 (1988).
- 10 T. S. Murthy, B. Rambabu, and K. Lakshminarayana, *Acoust. Lett.*, **17**, 111 (1993).