

CHAPTER - II

EXPERIMENTAL SECTION

(Materials and methods)

Chemicals

Tetraalkylammonium salts were of Fluka's purum or puriss grade and purified in the manner given in the literature^{1,2}. Generally the salts were purified by recrystallisation. The bromide salts of higher tetraalkyl homologues were recrystallised second time to ensure highest purity. The crystallised salts were dried in vacuum. The salts were stored in glass bottles in darkened desiccator over fused CaCl_2 .

Tetraethylammonium bromide (Et_4NBr) (Fluka, purum) was recrystallised from methanol and dried at 363K for 24 h.

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

Tetrabutylammonium bromide (Bu_4NBr) (Fluka, puriss) was taken in a minimum volume of acetone. Ether was added till the commencement of precipitation. The solution was then cooled and the resulting crystals were filtered in a sintered glass funnel. After a preliminary drying, the salt was finally ground in a mortar and dried at 333K for 48 h.

Tetrapentylammonium bromide (Pent_4NBr) (Fluka, puriss) was recrystallised from acetone + ether mixtures and dried in vacuo at 333K for 48 h.

Tetrahexylammonium bromide (Hex_4NBr) (Fluka, purum) was washed with ether and dried in vacuo at room temperature for three days.

Tetrabutylammonium tetraphenyl borate (Bu_4NBPh_4) was prepared by precipitation from Bu_4NBr and NaBPh_4 in water³. The salt was dried in vacuo at 353K for 48 hours.

Sodium tetraphenyl borate (NaBPh_4) (Fluka, puriss) was recrystallised from acetone and dried in vacuo at 353K for 72 hrs.

Tetrabutylammonium tetrabutyl borate⁴ (Bu_4NBu_4) (Alfa product) was dissolved in methanol, reprecipitated from water and dried in vacuo at 300K for 48 hrs.

Sodium bromide (NaBr) was of G.R.E. Merck grade and was used without further purification after drying at 400K.

Solvents

2-Methoxy Ethanol (ME) (G.R.E. Merck) was distilled twice in an all glass distillation set before use. The purified solvent had the density 0.86002 gm/c.c., viscosity 0.0154149 and the electrical conductance was 1.01×10^{-6} ohm⁻¹ cm⁻¹ at 25°C. The solvent was stored in dry box. The physical properties of the solvent (ME) are in conformity with the literature values⁵. Freshly distilled ME was always used for preparing the experimental solutions.

1,2-dimethoxy ethane (DME) (Fluka, purum) was first shaken with ferrous sulphate (FeSO_4) (AR, E.M.) for 1-2 hrs,

decanted and then distilled. The distillate was then successfully refluxed for 12 hours and distilled over metallic sodium. The boiling point and density compared fairly well with the corresponding values in the literature⁶ (b.p = 83.5°C, $d_0 = 0.86261 \text{ g cm}^{-3}$ at 25°C). The specific conductance of DMS was found to be $0.81 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C.

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 (TD) water had specific conductance less than $1 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$.

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% of 2-methoxy ethanol were prepared accurately by mixing the requisite amounts of H_2O and ME by weight. Solvent properties of ME - H_2O mixtures are given in Table 1. The dielectric constant values have been taken from the literature⁵. A plot of viscosity against mole fraction of ME is shown in Fig. 1.

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

| Wt% ME | ϵ | $\rho/\text{g cm}^{-3}$ | $\eta_0 \times 10^2 \text{ P}$ | Specific conductance ($\text{ohm}^{-1} \text{ cm}^{-1}$) |
|--------|------------|-------------------------|--------------------------------|---|
| 0 | 78.42 | 0.99707 | 0.8903 | $< 1.01 \times 10^{-6}$ |

Table 1 (Contd..)

| Wt% ME | ϵ | ρ/gcm^{-3} | $\eta_0 \times 10^2 P$ | Specific conductance ($\text{ohm}^{-1} \text{cm}^{-1}$) |
|--------|------------|------------------------|------------------------|--|
| 20 | 69.73 | 1.0024 | 1.51647 | 37.3×10^{-6} |
| 40 | 57.41 | 1.0059 | 2.36545 | 20.0×10^{-6} |
| 60 | 42.11 | 1.00233 | 2.88490 | 7.22×10^{-6} |
| 80 | 26.53 | 0.98572 | 2.57508 | 3.84×10^{-6} |
| 100 | 16.93 | 0.96002 | 1.5414 | 1.01×10^{-6} |

Preparation of the experimental solutions:

A stock solution for each salt ($\sim 0.1 \text{ M}$) in ME was prepared by weight and the working solutions were obtained by weight dilution. The concentration ranges of the working solutions were 0.01 - 0.05M. The molar concentration of the solutions were calculated from molality and density values.

The procedure for the preparation of solutions in mixed solvents was the same as before, only ME was replaced by the mixed solvent of the desired composition.

The concentrations for the conductance measurements varied between 0.0005 - 0.05M.

Methods: Density, Viscosity and conductance Measurements

(a) Densities were measured with a precision of 0.01% with an Ostwald-Sprengel type pycnometer (25 ml) calibrated with distilled water. The densities of the working solutions were obtained from equation (1)

$$\rho = \rho_0 + \theta \bar{m}^{7.8} \quad \dots (1)$$

where \bar{m} is the concentration in moles per kilogram of solutions, ρ_0 is the solvent density and θ is an empirical constant determined

by density measurements on the most concentrated solution studied for each salt. The experimental densities agreed well with those calculated using the equation (1).

(b) The kinematic viscosities were measured using a suspended level Ubbelohde Viscometer⁹ with a flow time of 538S for distilled water at 298K. The variation of efflux times were between 538S to 1835 secs over the range of concentrations of 0.01 to 0.05 m in the mixed solvents and MS.

The viscometer was calibrated with triple distilled water from the average flow times, t , and densities, ρ at two different temperatures. The equation (2) is used for the purpose

$$\eta/\rho = kt - \frac{L}{t} \quad \dots (2)$$

The absolute viscosity of water were taken from the literatures. The characteristic constant K and L of the viscometer were found to be 0.001648 and 2.331647 respectively. The calibration of the viscometer was periodically checked by measuring the flow times with water at two temperatures and the ratio K/L of the viscometer constants was found to be constant during the course of the work. A stop watch, was used for recording to flow time. Runs were repeated until three successive determinations were obtained within 0.1 S. The viscometer needs no correction for kinetic energy. Precautions were taken to obtain the viscometric values with an estimated precision better than 0.05%.

Relative viscosities η_{rel} were obtained using the equation (3)

$$\eta_{rel} = \eta/\eta_0 = \rho t/\rho_0 t_0 \quad \dots (3)$$

η , η_0 , ρ and ρ_0 are the viscosities, densities and t , t_0 are flow times for the solution and the solvent respectively where η and η_0 were calculated using equation (2).

(c) The conductance measurements of the solutions were made using a Philips PW 9509 conductivity bridge 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. The reproducibility of the conductance measurements were better than $\pm 0.2\%$.

The measurements were carried out in thermostatic bath controlled to $\pm 0.01^\circ \text{C}$ unless otherwise mentioned.

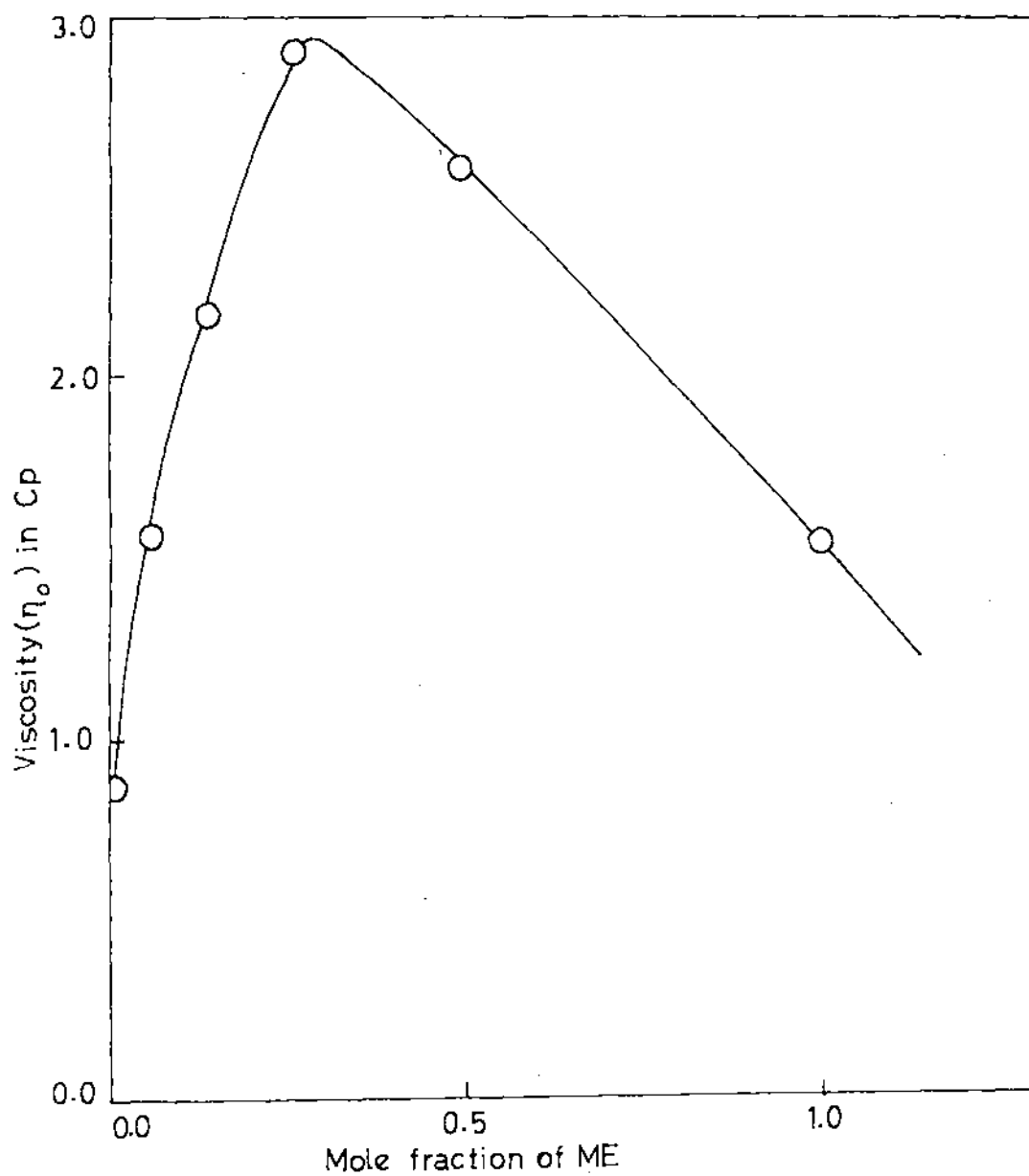


Fig.1 Variation of viscosity (η_0) with mole fraction of the solvent mixtures at 25° C

R E F E R E N C E S

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