

CHAPTER-II

EXPERIMENTAL SECTION

(Materials and Methods)

Chemicals

Alkali metal chlorides and bromides (Fluka, purum or puriss) were dried in vacuo for a long time immediately prior to use and were used without further purification.

Lithium perchlorate (LiClO_4 ; Fluka, > 99% pure) was recrystallized three times from deionised distilled water and dried under vacuum for several days¹. Sodium perchlorate (NaClO_4 ; AR, E. Merck, Germany) was recrystallized several times from water + methanol mixtures and dried in vacuo at 423 K for 96 hours. Other alkali metal perchlorates were prepared by mixing equimolar solutions of corresponding alkali metal chloride and sodium perchlorate, washed with 1:1 methanol-water mixture and then recrystallized thrice from water and dried in vacuum at 473 K over calcium chloride and silica gel for several days².

Tetraalkylammonium bromides (Fluka, purum or puriss) were purified in the manner given in the literature^{3,4}. 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 .

Tetramethylammonium bromide (Me_4NBr) was recrystallized from a 1:1 mixture of methanol-water and dried at 363 K for 48 hours⁴.

Tetraethylammonium bromide (Et_4NBr) was recrystallized 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 mortar and dried at 333 K for 48 hours.

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

Lithium tetrafluoroborate (LiBF_4 ; Fluka) was dried under vacuum at high temperatures for 48 hours and was used without further purification.

Sodium tetraphenylborate (NaBPh_4 ; Fluka, puriss) was recrystallized three times from acetone and dried in vacuum at 353 K for 72 hours.

Tetrabutylammonium tetrabutylborate (Bu_4NBu_4 , Alfa products) was dissolved in methanol, reprecipitated from water and dried in vacuum at 343 K⁵.

Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepared by precipitation from Bu_4NBr and NaBPh_4 in water and the precipitate was washed 5 times by water. The bulky white precipitate was dried and recrystallized four times from 1:3 water-acetone and finally dried for several days at 313 K under vacuum⁶.

Tetraphenylarsonium chloride (Ph_4AsCl , Fluka) was recrystallized from absolute ethanol solution by dry ether twice and dried in vacuum⁷.

Tetraphenylphosphonium bromide (Ph_4PBr ; Fluka, purum) was dissolved in ethanol, reprecipitated by the addition of dry ether and vacuum dried at 373 K⁷.

Solvents

Propylene carbonate (PC) (E. Merck, Germany; > 99% pure) was dried over freshly ignited quicklime for several hours⁸ and then distilled three times under reduced pressure under nitrogen, the middle fraction being taken each time. The purified sample had a density $1.19883 \text{ g cm}^{-3}$, a coefficient of viscosity 2.471 cP and a specific conductance $0.73 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C; these values are in good agreement with the literature values⁹, which are $1.19965 \text{ g cm}^{-3}$, 2.48 cP and $10^{-7} \text{ S cm}^{-1}$ respectively.

Methanol (E. Merck, India, uvasol grade) was dried over 3A molecular sieves and distilled fractionally. Middle fraction was taken and further distilled¹⁰. Physical properties of the purified sample at 25°C ($\rho = 0.79663 \text{ g cm}^{-3}$) and $\eta = 0.5437 \text{ cP}$) agree well with the literature values¹¹ which are : $\rho = 0.78664 \text{ g cm}^{-3}$ and $\eta = 0.5445 \text{ cP}$.

2-methoxyethanol (ME) (G.R.E. Merck) was distilled in an all glass apparatus. The physical properties at 25°C of purified ME were : density $0.96002 \text{ g cm}^{-3}$ and viscosity 1.5414 cP. The viscosity and density values are in reasonable agreement with the literature values¹¹ which are 1.60 cP and $0.96204 \text{ g cm}^{-3}$ respectively.

1,2-dimethoxyethane (DME) (Fluka, purum) was shaken well with FeSO_4 (AR, BDH) for 1-2 hours, decanted and distilled. The distillate was refluxed for 12 hours and redistilled over metallic sodium¹². The boiling point (84.5°C) and density (0.86132 gcm^{-3} at 25°C) compared fairly well with the corresponding literature values¹³, which are 85°C and 0.86120 gcm^{-3} respectively.

Tetrahydrofuran (THF) (E. Merck, India) was kept over KOH, refluxed for 24 hours and distilled over LiAlH_4 ¹⁴. The density (0.88072 gcm^{-3}) and viscosity (0.4630 cP) at 25°C of the purified sample are in good conformity with the literature values¹⁵, 0.8811 gcm^{-3} and 0.46 cP respectively.

Mixed Solvents

The mixed solvents containing 0.10, 0.20, 0.40 and 0.60 mole fractions of PC were prepared by mixing the requisite amounts of methanol and PC by weight. Solvent properties of PC + Methanol mixtures at 25°C are given in Table 1.

Table 1. Solvent properties of (PC + methanol) mixtures at 25°C.

Mole fraction of PC	ϵ	ρ/gcm^{-3}	η/cP	Sp. conductance Scm^{-1}
0	32.64	0.78663	0.5437	0.15×10^{-6} ^a
0.10	39.20	0.86928	0.6264	1.52×10^{-6}
0.20	44.10	0.93460	0.7192	1.81×10^{-6}
0.40	51.30	1.03274	0.9747	2.25×10^{-6}
0.60	57.30	1.10363	1.2972	2.42×10^{-6}
1.00	64.40	1.19883	2.4712	0.73×10^{-6}

^afrom ref. 10

Preparation of experimental solutions

A stock solution for each salt in PC 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-Sprengel 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 $\pm 3 \times 10^{-5} \text{ gcm}^{-3}$. The measurements were made in an oil bath maintained with an accuracy

of ± 0.005 °C of the desired temperature by means of a mercury in-glass thermoregulator and absolute temperature was determined by a platinum resistance thermometer and Muller bridge¹⁶.

(b) Viscosity measurement

The kinematic viscosities were measured by means of a suspended-level Ubbelohde¹⁷ viscometer with a flow time of about 539 s for distilled water at 25°C. 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 viscometer needed no correction for kinetic energy. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

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

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

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

Relative viscosities (η_r) were obtained using equation

(3):

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} \quad (3)$$

where $\eta, \eta_0; \rho, \rho_0$ 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 $\pm 0.01^\circ\text{C}$ of the desired temperature¹⁸. A 60W 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 $\pm 0.1\%$. 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. 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 $25 \pm 0.005^{\circ}\text{C}$ as described earlier under density measurements. All data were corrected with the specific conductance of the solvent.

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