

CHAPTER III

EXPERIMENTAL TECHNIQUES

3.1 Preparation of reagents and solvents

3.1.1 Electrolytes

a. Tetramethylammonium picrate The tetramethylammonium picrate was prepared by the method described in reference (12). A large amount of 5% aqueous picric acid solution which was recrystallized once from ethanol-water mixture prior to use was added to 20 cm³ of 10% aqueous solution of an A R grade tetramethylammonium hydroxide. The acid was added slowly with constant stirring until the solution became slightly acid. The solution was then made slightly basic upon the addition of few drops of the hydroxide solution. The reaction mixture was left overnight to ensure that all excess picric acid had reacted. The precipitate of tetramethylammonium picrate was filtered off and recrystallized six times from conductivity water-ethanol mixture, resulting in 1.5 g. of yellow needle crystals. The purity and properties of this salt were identified by means of IR-spectroscopy and paper chromatography.

b. Tetraethylammonium picrate First, tetraethylammonium hydroxide was prepared by mixing tetraethylammonium iodide with laboratory grade silver oxide (for the preparations of ethyl iodide, tetraethylammonium iodide and tetraethylammonium hydroxide see Appendix I).

The filtrate obtained was then treated with picric acid and the subsequent procedure follows the method of the preparation of tetramethylammonium picrate as described above, about 2 g. of tetraethylammonium picrate was obtained.

3.1.2 Solvents

a. Conductivity water The adequately pure conductivity water can be prepared by passing double distilled water to an ion exchange resin to give a final specific conductance of about 0.75×10^{-6} ohms⁻¹ cm⁻¹ at 25°C.

b. Dioxane The Merck extra pure dioxane whose purity was specified by manufacturer as containing 0.1% water and 0.005% hydrogen peroxide was used without further purification. The composition of dioxane-water mixture was prepared by weighing. Its dielectric constant was obtained from the literature.⁽¹³⁾ Typical values are shown in Table 3.3

c. Other solvents Other solvents were purchased at AR grade from BDH Chemicals Ltd. They are acetone, methanol, ethanol and cyclohexanone. Their specific conductances were measured at 25°C values of which were 1.03×10^{-6} , 7.8×10^{-6} , 1.84×10^{-6} and 0.0168×10^{-6} ohms⁻¹ cm⁻¹ respectively.

3.2 Apparatus

The major apparatus used in this work are listed below.

3.2.1 Conductivity bridge The Beckmann A.C. conductivity bridge with oscillator and detector type RC - 18A was used in this work. It is capable of producing accuracy up to $\pm 0.05\%$ of the decade resistance readings.

3.2.2 Conductance cell The Beckmann conductance cell Model CEL-36 (cell I) was used in conjunction with the conductivity bridge. Its cell constant is 0.0784207 at 1 KC/S and 0.0781498 at 3 KC/S as determined by the intercomparison method.⁽¹⁴⁾

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3.2.3 U.V. Spectrophotometer Ultra violet absorption spectra were recorded using a Varian Techtron Model 635 spectrophotometer. The cell holder and thermostat bath provided by the manufacturer enabled the spectrophotometric work to be done at the pre-set constant temperature. The usual conditions employed were as follows:

Light source	=	Visible
wavelength scan	=	500 - 280 nm
range	=	20 nm/cm (F)
scan rate	=	100 nm/min.
slit width	=	0.25 nm

3.2.4 Thermostat bath It is very important to have an accurate temperature control within the narrow range required both in a high precision conductance measurement and U.V. spectrophotometry. For conductance measurement the cell was immersed in the thermostat bath whose temperature can be controlled to within $\pm 0.01^{\circ}\text{C}$ by means of Beckmann contact thermometer. For spectrophotometry see 3.2.3.

3.2.5 Viscometer The viscosities of organic solvents used as the solvents in this work were measured by using Ostwald viscometer type M I No. 9205.

3.2.6 Balance Since small quantities of solutes were encountered in this work, a Mettler type M 5 microbalance with 20 g. capacity and ± 0.02 mg. accuracy was used for weighing of tetramethyl and tetraethylammonium picrates. As for solvents and other reagents, a Mettler type H-20 semimicrobalance with 161 g. capacity and ± 0.1 mg. was used throughout.

3.3 Conductivity measurements

3.3.1 Determination of cell constant Cell constant of cell I was determined by intercomparison with cell II, Beckmann conductivity cell Model CEL-3 B, having 0.01 N potassium chloride as an electrolyte solution, at 25°C whose specific conductance was $0.0014087 \text{ ohm}^{-1} \text{ cm}^{-1}$ (15). The values obtained by this method are shown in Tables 3.1. and 3.2.

Table 3.1.

Cell constant of cell II

Cell type	KCl (demal)	$1/R_{\text{corr}} \times 10^6 (\text{ohm}^{-1})$		$L \times 10^6$ ($\text{ohm}^{-1} \text{ cm}^{-1}$)	Cell constant	
		1 Kc/S*	3 Kc/S		1 Kc/S*	3 Kc/S
II	0.01	627.57	629.06	0.0014087	2.2451046	2.2408135

1 Kc/S* = 1 Kilocycle per second

Table 3.2

Cell Constant of Cell I by Intercomparison Method

KCl (equi/l)	$1/R_{\text{corr}} \times 10^6$ (ohms ⁻¹)				$L \times 10^6$ (ohms ⁻¹ cm ⁻¹)		cell constant	
	cell I		cell II		cell II		cell I	
	1 kc/s	3 kc/s	1 kc/s	3 kc/s	1 kc/s	3 kc/s	1 kc/s	3 kc/s
0.0009995	66.70	66.45	1913.12	1915.12	149.75386	148.92078	0.0782773	0.0777573
0.0014993	100.35	99.65	2869.41	2857.18	225.31121	223.3063	0.0785216	0.0781562
0.00199	132.21	131.36	3815.75	3785.75	296.82375	294.35379	0.0777891	0.0777531
0.0024988	164.66	163.84	4662.96	4654.50	369.69672	367.14277	0.0792837	0.0788791
0.0029986	193.40	191.53	5550.20	5488.00	434.20769	429.18080	0.0782319	0.0782035
Average							0.0784207	0.0781498

3.3.2 Measurement of conductivity of unassociated electrolytes

All measurements were made with cell I at 1,000 cycle per second. After being cleaned with the cleaning solution the cell was rinsed with distilled water, conductivity water and finally with acetone and dried. To avoid the error due to dilution effect the filling of the cell with the solution to be measured was done only after rinsing the cell with the same solution several times.

The solution was prepared by mixing a quantity of tetramethyl or tetraethylammonium picrate and the 80% dioxane-water mixture which was kept at the studied temperature before use. The conductance was recorded soon after mixing, within 3 minutes. The conductances of tetramethyl and tetraethylammonium picrates in 80% dioxane-water mixture at various concentration, various time but at constant electrolyte solution ($8.95 \times 10^{-5}M$) were measured at 25° , 30° , 35° and $40^{\circ}C$. The variations of conductance with time were recorded at 5 - 10 minute interval until equilibrium was attained. Each recorded value was undergone the so called solvent correction ⁽¹⁶⁾ as usual.

3.3.3 Determination of limiting equivalent conductance The limiting equivalent conductance of tetramethyl and tetraethylammonium picrates in 80% dioxane-water mixture at 25° , 30° , 35° and $40^{\circ}C$ was obtained indirectly by making use of the Walden's Rule (see Appendix II). The required conductances and viscosities of both electrolytes at dilute concentration $3.3112 \times 10^{-6}M$ in conductivity water, methanol, acetone, ethanol and cyclohexanone were measured. Results are shown in Tables 4.2.1, 4.2.2, 4.2.3 and 4.2.4.

3.4 U.V. Spectrophotometry

The absorbances of tetramethyl and tetraethylammonium picrates in 80% dioxane-water mixture as a function of time were measured at constant maximum wavelength and constant concentration. The solutions and solvents under study were filled in the Optical Varian Techtron cells type CYI which were put in the cell holder immersed in the thermostat bath controlled at constant temperature i.e., 30°C. The absorption spectra and results are shown in Figures 5.2.1 and 5.2.2.

Table 3.3

Interpolated values for dielectric constant of a series
of dioxane-water mixture at various temperatures. (13)

dioxane % wt. t °C	0	10	20	30	40	50	60	70	80	90	95	98	100
0	88.31	78.86	69.16	59.34	49.37	39.50	29.84	20.37	12.19	6.16	3.91	2.73	2.109
10	84.25	75.06	65.68	56.24	46.71	37.51	28.17	19.25	11.58	5.93	3.82	2.70	2.104
20	80.37	71.43	62.38	53.30	44.19	35.25	26.60	18.20	10.99	5.71	3.74	2.68	2.102
30	76.73	67.98	59.24	50.52	41.80	33.30	25.12	17.20	10.44	5.50	3.65	2.65	2.100
40	73.12	64.70	56.26	47.88	39.54	31.46	23.72	16.26	9.91	5.30	3.57	2.62	2.098
50	69.85	61.57	53.43	45.38	37.41	29.72	22.40	15.37	9.41	5.10	3.49	2.60	2.096
60	66.62	58.60	50.75	43.01	35.39	28.08	21.15	14.52	8.93	4.91	3.41	2.57	2.094
70	63.50	55.77	48.20	40.76	33.48	26.52	19.97	13.73	8.48	4.73	3.33	2.55	2.092
80	60.58	53.07	45.77	38.63	31.67	25.05	18.86	12.97	8.05	4.56	3.25	2.52	2.090