

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Conductivity Water. The conductivity water was prepared by the first double distilling the tap-water using "Double Distillation Water Still Model 3 DWS" manufactured by James A Jobling Co. Ltd., followed by deionisation through the "Elgastat type B 114" unit. The specific conductance of this water is usually between 1.0×10^{-6} and $8 \times 10^{-7} \Omega \text{ cm}^{-1}$.

3.1.2 Chemicals. Crystalline KCl , ZnCl_2 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$ were used without further recrystallisation to prepare stock solutions. The dry salts which were stored in a desiccator at least for a week were used to make up stock solutions. The concentration of the stock solutions were further analysed.

KCl B.D.H. Analar KCl was used to prepare KCl solution for the determination of cell constants.

ZnCl₂ Merk Analar ZnCl_2 with 99.8% purity was used to prepare ZnCl_2 solution.

ZnSO₄·7H₂O. B.D.H. Analar $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ with 99.5% purity was used to prepare ZnSO_4 solution.

CdSO₄·8/3H₂O. Fluka Purrisss $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$ with 99.0% purity was used to prepare CdSO_4 solution.

Zn(ClO₄)₂. The stock $\text{Zn(ClO}_4)_2$ solution of about 3 mol kg^{-1} was prepared directly by the method in reference (9). The slight excess of Merk extra pure ZnO with 99.0% purity was added to 70% B.D.H. Analar HClO_4 and the unreacted oxide was filtered off.

3.2 Stock Solution and Their Analyses

Stock ZnCl_2 solution of about 0.5 mol kg^{-1} was prepared by dissolving the dry salt in deionised water. The concentration of the stock

solution was determined by the conductometric analysis using Paterson's equation (13), viz,

$$K = 2.315346 + 171.9464 \times C - 119.1111 \times C^2 + 32.0959 \times C^3$$

$$(0.3 \leq C \leq 0.7)$$

This solution was also determined by gravimetric silver chloride method. The two results agreed within $\pm 0.05\%$.

Stock $ZnSO_4$ solution of about 0.37 mol kg^{-1} was prepared by dissolving the salt in deionised water. The concentration of stock solution was determined by the gravimetric zinc sulfate analysis (10). The mean deviation over five analyses of the stock solution was about $\pm 0.05\%$.

The stock $Zn(ClO_4)_2$ solution was gravimetrically analysed (8) by adding sulfuric acid to weighed aliquots and evaporating to fumes of SO_3 . The residues were dried and weighed as $ZnSO_4$. The mean deviation over four analyses of the stock solution was about $\pm 0.05\%$.

Stock $CdSO_4$ solution of about 0.33 mol kg^{-1} was prepared by dissolving the dry salt in deionised water. The stock solution was determined by the gravimetric cadmium sulfate analysis (17). The mean deviation over four analyses of the stock solution was about $\pm 0.05\%$.

3.3 Preparation of Solutions

Weighings. All weighings were carried out at the laboratory temperature of about 28°C . Buoyancy corrections (18) were applied to all masses.

Solutions of the desired concentrations were prepared by weight dilution of the appropriate amounts of the stock solutions with deionised water. For dilute solutions, an accurately weighed amount of a suitable solution of known concentration was added quantitatively from the weight pipette (as shown in Fig 3.1) into the flask followed by the addition of the appropriate amount of deionised water to give the desired concentration.

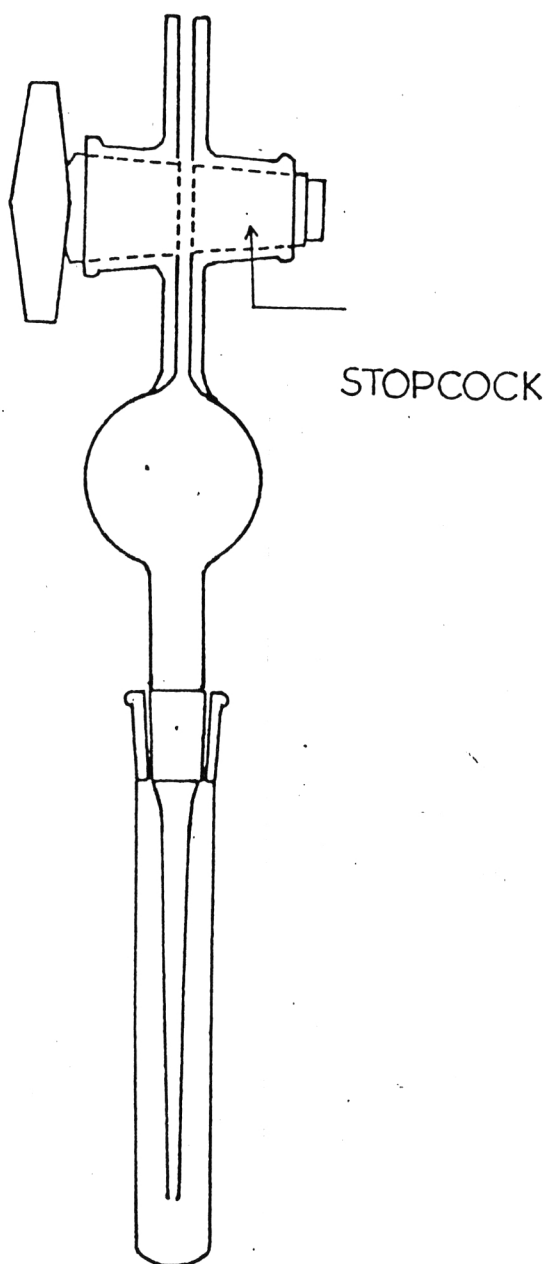
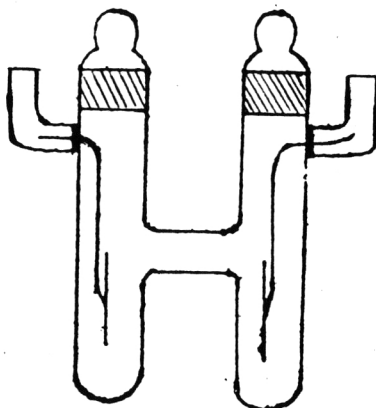


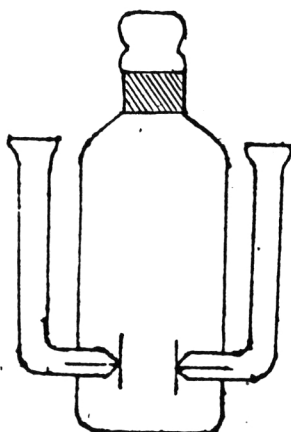
Fig 3.1 Weight pipette

Fig. 3.2 Diagram of conductance cells

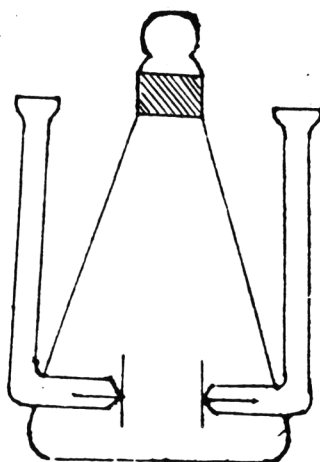
cell A.



cell B.



cell C.



3.4 Apparatus

3.4.1 Conductivity Bridge. A complete assemble of the A.C. conductivity bridge with oscillator and detector, Type "RC 18A" manufactured by Beckmann Instruments, Inc. was used in this work. The resistance has the total value of 111,111 Ω in steps of 0.1 Ω . The accuracy of the decade resistance readings over range 500-50,000 Ω is about $\pm 0.05\%$.

3.4.2 Conductivity Cells. Three types of the conductivity cells shown in Fig 3.2 were used in this work. Their use depends on the concentration of the solution under investigation. All the cells were constructed of pyrex glass to minimise adsorption between the solution and the cell walls.

Cell A was usually employed for measurements on solution of moderately high concentration while cells B and C were used for solutions of low concentration.

3.4.3 Temperature Control Unit. It is usually important to have a good temperature control for precised conductivity measurements. In this work the temperature of the solution was controlled by immersion of the cells in an electrically operated water filled thermostat bath. The temperature of thermostat bath was set accurately at 25.00 ± 0.01 °C by means of a Beckmann contact thermometer which remained constant to ± 0.01 °C. All measurements were carried out in an air-conditioned room with controlled temperature at about 25 °C. The calibrated A.S.T.M. thermometer R 37382 with the range 19 to 35 °C, graduated in 0.02 °C, was used to measure the thermostat temperature. Its calibration with a standard thermometer from National Physical Laboratory K.K showed that a temperature of 25.00 °C corresponds to the thermometer reading of 25.05 °C

3.5 Density Measurement

The densities of all solutions were determined at 25.00 ± 0.01 °C using a 10-cm³ pycnometer. Buoyancy corrections (18) were applied to all masses. The volumes of the pycnometer V_p , were determined from the density measurements of deionised water at 25.00 °C. Using $D_{H_2O}^{25} = 0.997044$, the results obtained from seven calibrations are,

$$V_p = 10.0023 \pm 0.0001 \text{ cm}^3$$

Plots of the densities of solutions are given in Figs 3.3, 3.4, 3.5, and 3.6 in Appendix A. Curve fitting of the data provide the density equation as listed in Table 3.1

Table 3.1

The Density Equations of Some Dilute Electrolyte Solutions

Electrolytes	Density at 25 °C / gm cm ⁻³	Concentration range/weight %
ZnCl ₂	$d^{25} = 0.997044 + 0.00923076 W$	0-0.4
	$d^{*25} = 0.997044 + 0.008958 W$ $- 0.00928571 W^2$	0.5-1.3
Zn(ClO ₄)	$d^{25} = 0.997044 + 0.0071439 W$	0-2.7
ZnSO ₄	$d^{25} = 0.997044 + 0.0102283 W$	0-1.4
CdSO ₄	$d^{25} = 0.997044 + 0.00964231 W$	0-2.2

* From the analysis of the density data of this system, the plot of $(d_{\text{ZnCl}_2}^{25} - d_{\text{H}_2\text{O}}^{25})W_{\text{ZnCl}_2}$ VS. W_{ZnCl_2} gave a straight line with the intercept and slope at 8.958×10^{-3} and 9.28571×10^{-4} , respectively.

W is the weight percent of the electrolytes.

3.6 Conductivity Measurements

3.6.1 Experimental Procedure

All measurements were made in the conductivity cells held in a thermostat bath maintained at $25.00 \pm 0.01^\circ \text{C}$. The resistance measurements were observed at 1000 and 3000 cycles per second. When frequency dependence resulted, the value of R was obtained by plotting the observed resistances with reciprocals of frequencies, and extrapolating them to an infinite frequency. The cells were thoroughly cleaned with

dichromic-sulfuric acid mixture, followed by rinsing with distilled water, then with conductivity water. The cells must be filled with conductivity water when not in use.

In the commencing of the measurement the cell was rinsed at least three times with the desired solutions, after which was refilled with the appropriate solution and immersed in the thermostat bath, where it attained thermal equilibrium for about 1/2 hour. The resistance was measured at 5 minute intervals in a series of 3-10 readings until the constant value was obtained.

After the first set of measurements was made, the solution filled cell was shaken and the measurement was repeated in the case of dilute solutions. This additional shaking had been found to eliminate the Soret effect (19). For moderately dilute solutions, it was found necessary to carry out 2-3 successive measurements after the cell had been refilled with the same solution.

3.6.2 Determination of Cell Constants

The cell constants were determined using the method of Jones and Bradshaw (20) by measuring the conductivity of standard 0.01 N KCl solution. The value of the specific conductance in Table 3.2 was used to calculate the cell constants from the relationship:

$$\text{specific conductance} = (\text{observed conductance} - \text{solvent conductance}) (\text{cell constant})$$

Because of the low cell constants, cell B and cell C were also determined by intercomparison with the cell whose cell constant was accurately known (21) and by the methods mentioned in reference (22). These methods gave results agree within $\pm 0.05\%$. The values of the cell constant are shown in Table 3.3.

Table 3.2
Specific Conductance of Potassium Chloride Solutions

Solution (demal)	g of KCl per 1000 g of Water	Specific Conductance ($\Omega^{-1} \cdot \text{cm}^{-1}$)		
		0 °C	18 °C	25 °C
1.0	76.627	0.06517	0.09783	0.11134
0.1	7.4789	0.007137	0.01116	0.012856
0.01	0.4789	0.007736	0.0012205	0.0014087

Table 3.3
Cell Calibration

Type of Cell	Cell Constant/cm ⁻¹
A	4.551 ₅ ± 0.002
B	0.1976 ₆ ± 0.0001
C	0.1600 ± 0.0001

3.6.3 Calculation of the Conductance

From the resistance measurements, the conductivity was calculated using equation 1.

$$\kappa_{\text{obs}} = \frac{b}{R} \quad (1)$$

where κ_{obs} is the observed value, and b is the cell constant. This conductivity was corrected for solvent conductivity by equation 2.

$$\kappa = \kappa_{\text{obs}} - \kappa_{\text{solvent}} \quad (2)$$

3.6.4 Conductivities of the Solutions

Results of the conductivity of aqueous $\text{Zn}(\text{ClO}_4)_2$, ZnSO_4 , ZnCl_2 , and CdSO_4 solutions at various concentrations are listed in Tables 3.4, 3.5, 3.6, and 3.7 respectively. A plot of Λ as a function of $C^{1/2}$ will be shown in the later Chapter.

Table 3.4

Conductivity of Zinc Perchlorate in Aqueous Solvent

$m \times 10^4$ mol kg ⁻¹	W (weight %)	$M \times 10^4$ mol dm ⁻³	Λ cm ² Ω ⁻¹ equiv ⁻¹
1042.69	2.6816	1031.17	88.87
858.651	2.2188	850.042	90.42
663.185	1.7224	657.854	92.39
505.356	1.3179	501.916	94.30
345.501	0.9035	343.093	96.99
294.472	0.7722	292.945	99.10
184.919	0.4863	184.114	100.96
156.016	0.4106	155.371	102.53
139.499	0.3673	138.939	102.96
119.845	0.3157	119.382	103.83
99.905	0.2633	99.534	105.42
85.517	0.2255	85.208	106.85
69.605	0.1836	69.362	108.16
54.025	0.1426	53.843	109.04
35.201	0.0929	35.087	111.29
13.745	0.0363	13.702	115.24
10.702	0.0283	10.672	115.63
6.512	0.0172	6.493	117.13
4.662	0.0124	4.648	117.47
2.537	0.0067	2.529	118.23

Table 3.5
 Conductivity of Zinc Sulfate in Aqueous Solvent

$m \times 10^4$ mol kg ⁻¹	W (weight %)	$M \times 10^4$ mol dm ⁻³	Λ cm ² Ω ⁻¹ equiv ⁻¹
888.448	1.41395	878.054	46.42
875.759	1.39404	865.623	46.58
786.972	1.25448	778.551	47.64
585.119	0.93572	580.020	50.89
488.706	0.78275	484.911	52.53
387.510	0.62376	386.420	55.54
291.856	0.46893	290.155	58.89
196.405	0.31605	195.444	64.33
153.569	0.24762	153.125	67.82
99.802	0.16085	99.408	74.45
92.459	0.14903	92.100	75.21
68.490	0.11044	68.240	79.69
58.946	0.09506	58.737	81.93
49.300	0.07952	49.129	84.85
39.202	0.06324	39.070	88.33
28.553	0.04607	28.460	93.14
19.929	0.03216	19.865	98.43
10.673	0.01722	10.639	106.57
7.659	0.01236	7.635	110.77
5.263	0.00849	5.246	114.49
3.368	0.00543	5.357	118.44

Table 3.6

Conductivity of Zinc Chloride in Aqueous Solvent

$m \times 10^4$ mol kg ⁻¹	W (weight percent)	$M \times 10^4$ mol dm ⁻³	Λ cm ² Ω ⁻¹ equiv ⁻¹
989.811	1.33096	983.784	76.15
942.381	1.26799	936.863	77.24
853.739	1.15009	849.096	78.71
753.226	1.01606	749.426	81.58
744.741	1.00473	741.018	81.87
635.973	0.85925	633.061	84.79
502.102	0.67961	500.028	88.75
483.823	0.65503	481.866	89.50
374.308	0.50751	372.910	93.53
288.313	0.39137	288.353	97.12
187.603	0.25501	187.004	103.69
92.1240	0.12538	91.8431	109.89
89.7090	0.12210	89.4367	110.22
86.5610	0.11782	86.2968	110.55
82.9609	0.11294	82.7097	111.11
80.7726	0.10995	80.5271	111.26
56.7285	0.07724	56.5587	114.60
47.3817	0.06452	47.2391	116.20
34.4434	0.04691	34.3406	118.18
27.5286	0.03750	27.4459	119.74
22.0652	0.03006	21.9152	121.14
19.2091	0.02617	19.1521	121.70
12.8744	0.01754	12.8362	123.18
3.05319	0.00416	3.04413	127.81

Table 3.7
 Conductivity of Cadmium Sulfate in Aqueous Solvent

$m \times 10^4$ mol kg ⁻¹	W (weight %)	$M \times 10^4$ mol dm ⁻³	Λ cm ² Ω^{-1} equiv ⁻¹
1065.118	2.1721	1060.725	40.94
993.387	2.0298	989.872	41.65
874.378	1.7901	871.008	42.90
772.176	1.5842	769.304	44.16
628.144	1.2925	625.919	46.49
547.070	1.1276	545.182	47.53
431.743	0.8920	430.307	50.65
326.289	0.6756	325.237	54.10
225.424	0.4678	224.718	59.05
123.173	0.2561	122.797	67.90
98.207	0.2043	97.909	71.26
87.782	0.1826	87.516	72.95
66.123	0.1376	66.031	77.63
65.212	0.1357	65.015	77.87
55.622	0.1158	55.454	80.68
41.826	0.0871	41.700	85.11
32.549	0.0678	32.451	89.29
24.857	0.0518	24.782	93.60
10.471	0.0218	10.439	106.33
8.853	0.0184	8.826	108.49
8.256	0.0172	8.230	109.48
6.941	0.0145	6.919	111.50
5.273	0.0110	5.256	114.25
4.667	0.0097	4.652	116.05
3.535	0.0074	3.523	118.22