



CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Conductivity water The conductivity water was prepared by first double distilling the tap-water using " Double Distillation Water Pyrex Still Model 3DWS " manufactured by James A Jobling Co. Ltd., following by deionisation through the "Elgastat" unit type B114. The specific conductance of water is usually $1.005 \times 10^{-6} - 1.010 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$.

3.1.2 KCl B.D.H.Analar KCl, not less than 99.8 %purity was used without recrystallisation. The salt was dried above 100°C to constant weight.

3.1.3 ZnCl₂ Merk Zur Analyse ZnCl₂ with 99.8 % purity was used without recrystallisation. The dry salt was used to make up a stock solution.

3.1.4 HCl Concentrated Riedel De Haenag fur Analyse Hydrochloric acid of 37% composition was used to prepare the solution without further purification.

3.1.5 Zinc rod The zinc rod obtained from Fluka AG of Switzerland with 99.99% purity was used as an anode.

3.2 Apparatus

3.2.1 Conductivity Bridge

A complete assemble of the A.C. conductivity bridge with oscillator, type " RC 18A ", manufactured by Beckmann

Instruments, Inc., was used to make conductance measurements throughout this work. The resistance can be measured with the range 0 - 111,111 Ω and gives the results accurate about $\pm 0.05\%$ of the decade resistance readings over range 500 - 50,000 Ω .

3.2.2 Conductivity Cell

Three types of the conductivity cells as shown in Fig 3.1 were used in this work. All the cells were made of pyrex glass to minimise adsorption between the solution and the cell walls.

3.2.3 Indirect Moving Boundary Cell

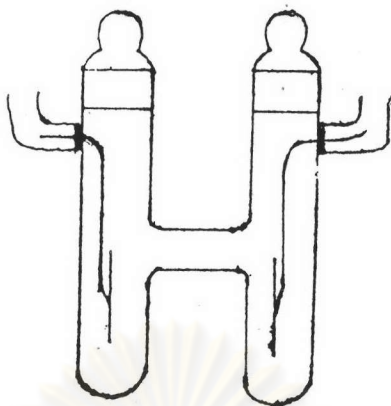
The indirect moving boundary cell used in this work is the same as that developed by Indaratna (14). It consists of the main body of the cell, the removable cathode, and anode units. All parts are made of pyrex glass to reduce the solvent correction arising from the adsorption and leaching of electrolytes between the glass walls and the solutions.

A diagram of the complete transference number cell is shown in Fig 3.2. The bore of the stopcock was the same size as the rest of the tubing. The ends of the stopcock was cut open, as shown in Fig 3.3, leaving hollow barrels. This allows free circulation of the thermostat liquid which prevents local heating. The dimension of the cell is given in Table 3.1.

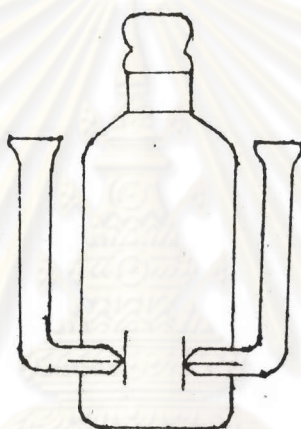
A separate H shaped pyrex glass vessel shown in Fig 3.4 served as a cathode unit which was connected to the top of the moving boundary cell by a ground glass joint. The anode unit consists of a closed anode compartment at the lower end of the boundary cell fitted with an appropriate electrode plug.

Fig. 3.1 Diagram of conductance cells

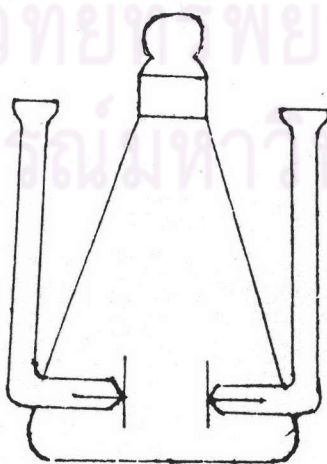
cell A.

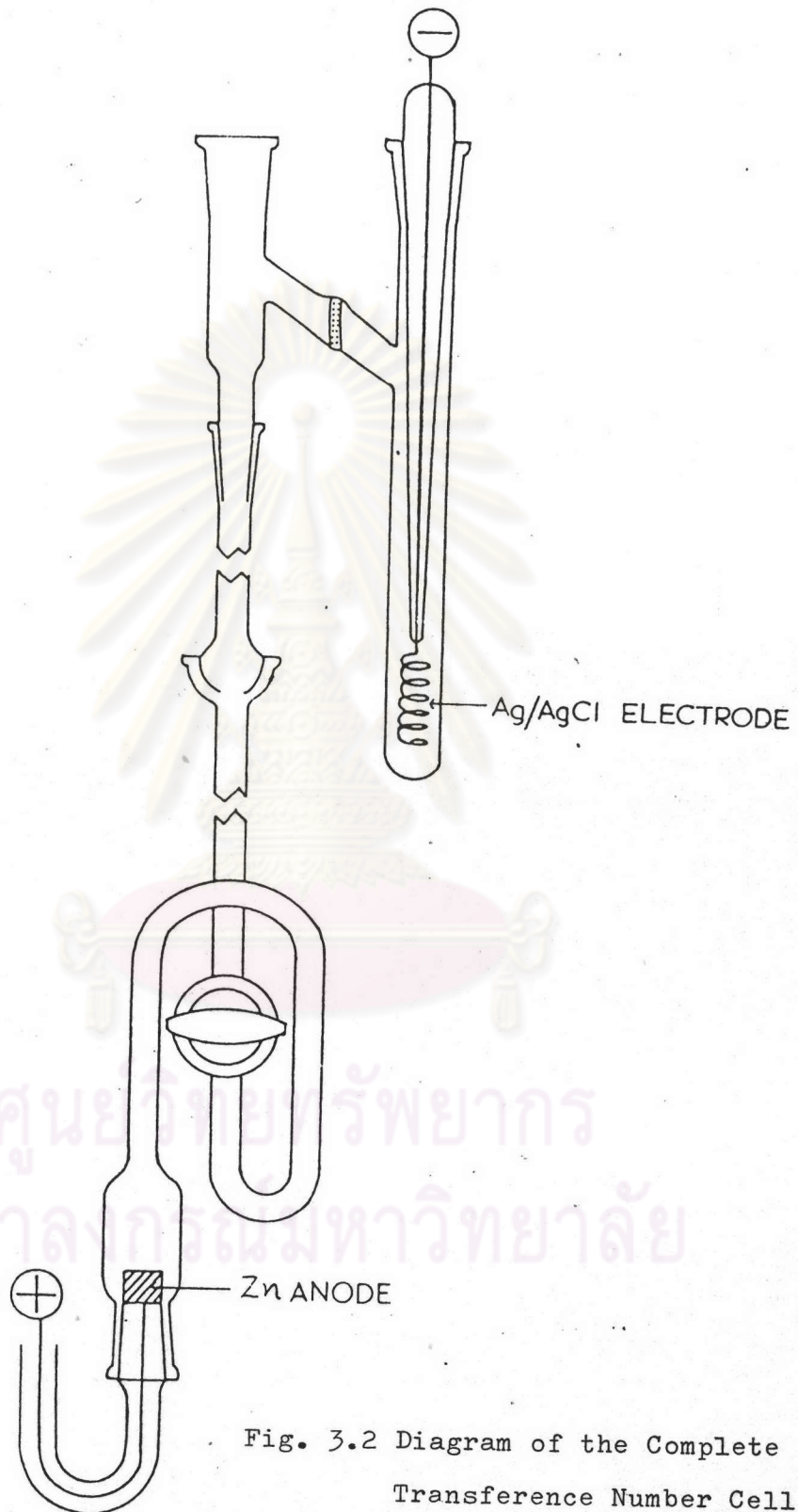


cell B.



cell C.





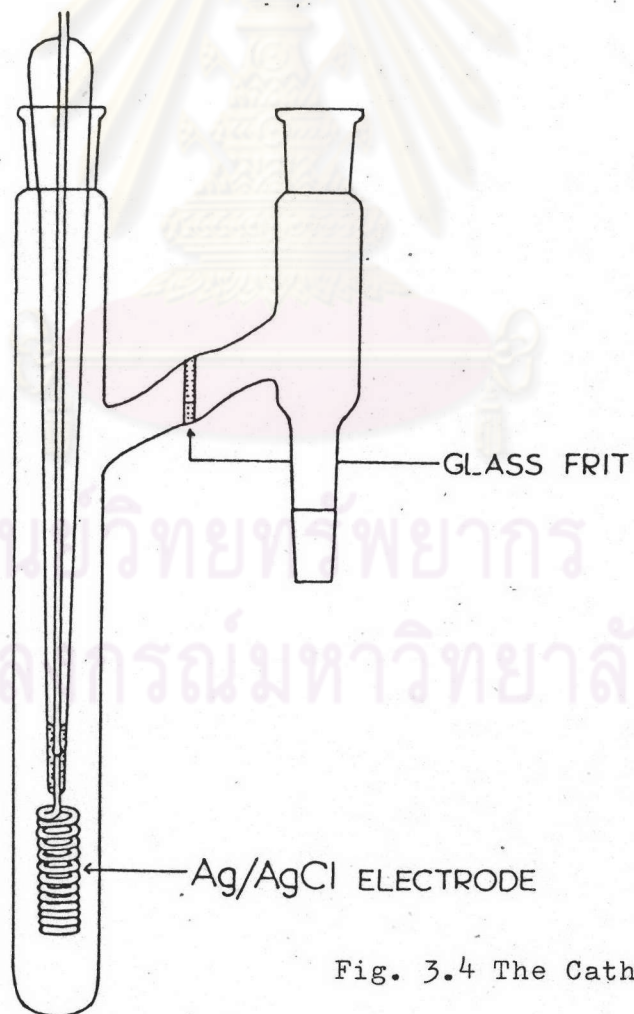
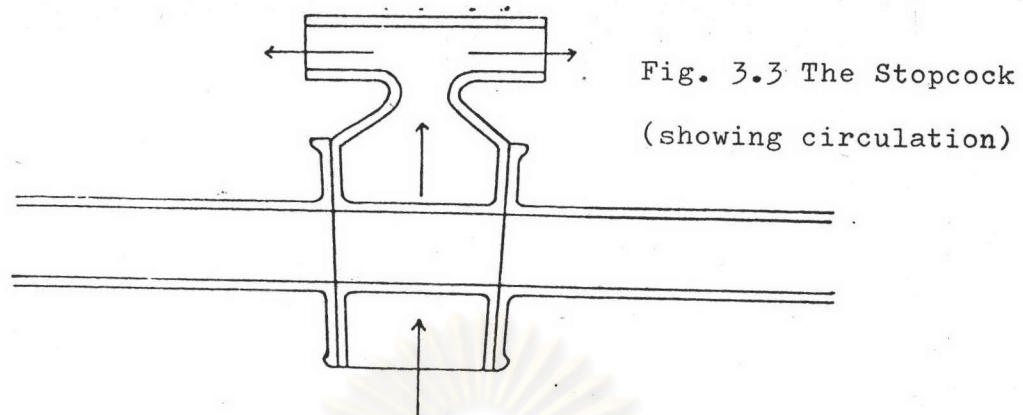


Fig. 3.4 The Cathode Unit

Table 3.1 Dimensions of the Transference Number Cell

Bore Size i.d./mm	Middle Section A-B length/cm	Anode-B length/cm	J-A length/cm	Total Cell length/cm
5	28.5	23.0	10.0	45.0

A refers to ball and cup joint

B refers to stopcock

J refers to top of the cell

3.2.4 Temperature Control Unit

It is very important to have an accurate temperature control within the narrow range required for high precision conductivity and transference number measurements. The temperature of the solution measured was controlled by immersion of the cell in an electrically operated thermostat bath filled with water. The temperature of thermostat bath was regulated by means of a Beckman contact thermometer set accurately at $25.00 \pm 0.01^\circ \text{C}$. The A.S.T.M. thermometer R 37382 with the range 19° to 35°C , graduated in 0.02°C , was used for temperature reading. It was calibrated with a standard thermometer from National Physical Laboratory K.K. At 25.00°C of the standard thermometer, this thermometer reads $25.05 \pm 0.01^\circ \text{C}$.

For transference number determination, an additional water jacket was required to accommodate the whole length of the moving boundary cell. A top-cut plexi glass cylinder partially immersed in the glass water tank was used. Circulation of the thermostat water through this vessel was achieved by a

glass centrifugal pump. This pump was immersed in the water bath with all the chambers filled with water. Rotation of the 3 way glass tubing by a stirrer motor produced centrifugal force which generated flows. The temperature in the water jacket was set accurately at $25.00 \pm 0.01^{\circ} \text{C}$

3.2.5 A Current Regulator

In this work, a current regulator with the range 1 - 10 milliamps, designed by Mr. Somchai Pisolyaboot of the Department of Chemistry, Chulalongkorn University, was used. This current regulator can supply up to 300V d.c. and 10 mA.

3.3 Solution Preparation and Concentration Determination

3.3.1 Stock Solutions and Their Analyses

Stock zinc chloride solution of about 0.5 mol kg^{-1} was prepared by dissolving the salt in deionised water. The concentration of the stock solution was determined by the conductometric analysis using Paterson's (17) equation, viz,

$$K = 2.315346 + 171.9464 M - 119.1111 M^2 \quad (0.3 < M < 0.7)$$

and was redetermined by gravimetric method (38). The two results agreed within $\pm 0.05 \%$.

Stock hydrochloric acid solution of about 0.5 mol kg^{-1} was prepared by weight dilution of the concentrated analysed HCl solution. The concentration of the stock was determined by the conductometric analysis developed by R.H. Stokes (39). Detail of this calculation can be found in Appendices 1,2,3.

3.3.2 Preparation of Solutions by Weight Dilution

Solutions of the desired concentrations were prepared by weight dilution of the appropriate amounts of the stock solutions with deionised water. Bouyancy correction (40) were applied to all masses.

3.4 Preparation of the Electrodes

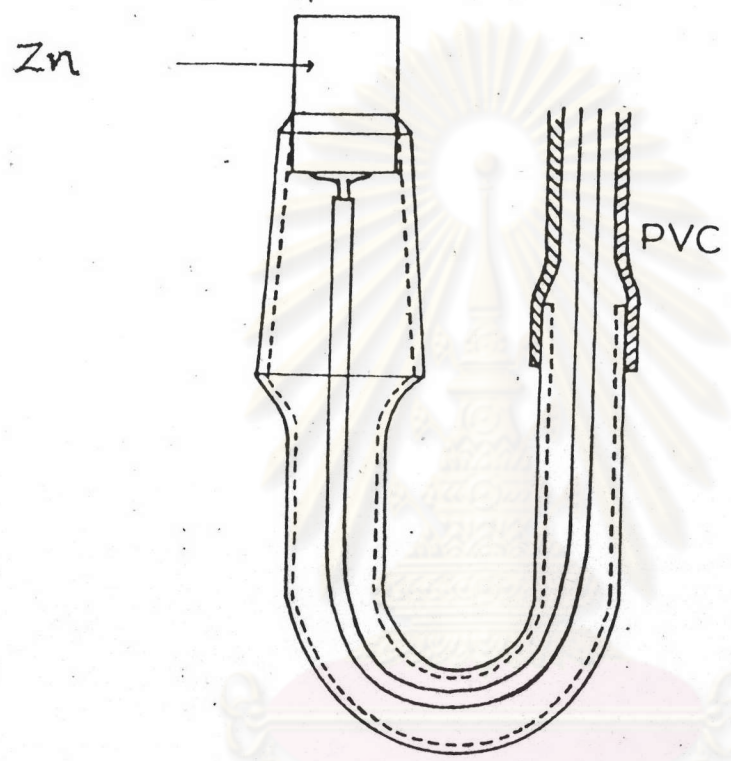
3.4.1 Silver - Silver Chloride Electrodes

Silver - silver chloride electrodes were used as cathodes. The copper wire was sealed into glass tubing with the outer end joined to a 1 mm i.d. silver wire. An appropriate amount of silver was converted to silver chloride by passing a current of about 0.5 to 1 mA between the silver and platinum electrode in 1 mol kg⁻¹ hydrochloric acid. The electrode was initially stored in deionised water over night to allow hydrochloric acid to diffuse out and was kept immersed in the leading solution before use.

3.4.2 Zinc Anode

The anode unit shown in Fig 3.5 was made by sealing a Zinc rod fitted with a copper wire lead into an appropriate ground glass cone with " Araldite " epoxy resin. The glass tubing below the cone was bent to a U shape connected with the rubber base. The other end of this glass tubing was connected to long p.v.c. tubing which extended above the thermostat liquid and provided additional insulation for the electrical lead. Before use, the zinc anode surface was cleaned by immersion in 2 mol kg⁻¹ nitric acid then it was rinsed several times with deionised water and dried with tissue paper.

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Fig. 3.5 The Zinc Anode Unit

3.5 Conductivity Measurements

3.5.1 Experimental Procedure.

All measurements were made in conductance cells held in a thermostat bath maintained at 25.00 ± 0.01 C. The resistance was observed at the oscillator frequency of 1000 and 3000 cycles per second. The conductance cells were thoroughly cleaned with dichromic - sulfuric acid mixture, followed by rinsing with distilled water, then with deionised water. The cells were filled with deionised water when not in use.

The cell is 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. The resistance is measured at 5 minute intervals in a series of 4 - 10 readings. When frequency dependence resulted, the value of R was obtained by plotting the observed resistances with reciprocal of frequencies, and extrapolating them to an infinite frequency.

After the first set of measurements was made, the solution filled cell was shaken and the resistance measurement was repeated. This additional shaking had been found to eliminate the Soret effect (41), which was observed in the case of dilute solutions. 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.



3.5.2 Determination of Cell Constants

The cell constants were determined, using the method of Jones and Bradshaw (42) by measuring the conductivities of standard 0.01D KCl solution. The value of the specific conductance in Table 3.2 was used to calculate the cell constants.

Table 3.2 Specific Conductivities of KCl Solutions

Solutions	g KCl/1000g solutions (in vacuo)	K($\Omega^{-1}\text{cm}^{-1}$)		
		0°C	18°C	25°C
1D	71.352	0.06517 ₆	0.09783 ₈	0.11134 ₂
0.1D	7.41913	0.007137 ₉	0.011166 ₇	0.012856 ₀
0.01D	.745263	0.0007736 ₄	0.0012205 ₂	0.0014087

Because of the low cell constants, cell B and C were also determined by intercomparison with the cell whose cell constant is accurately known (43) and by the methods mentioned in reference (44). The three methods gave results which agree within $\pm 0.05\%$. The values of the cell constants are shown in Table 3.3.

Table 3.3 Cell Calibration

Type of Cell	Cell Constant/ cm^{-1}
A	4.511 ₅ \pm .002
B	0.1977 \pm .0001
C	0.1600 \pm .0001

3.5.3 Conductivity of Zinc Chloride in Aqueous Solutions

The conductivities of aqueous ZnCl_2 solutions at various concentrations were measured by the conventional technique mentioned above. For the solutions of high concentration, the conductance measurements were made in the conductance cell A. The conductance cell B and C were used for the solution of moderate and low concentration.

3.5.4 The Calculation of the Conductance

From the resistance measurements, the conductivity was calculated using equation (3.1)

$$K_{\text{obs}} = \frac{b}{R} \quad (3.1)$$

where K_{obs} is the observed conductivity of the solution, and b is the cell constant. Applying the solvent correction, thus the conductivity was calculated from equation (3.2)

$$K = K_{\text{obs}} - K_{\text{solvent}} \quad (3.2)$$

3.6 Determination of the Transference Number

3.6.1 Experimental Procedure

After removal of all joint and stopcock grease with hexane solvent the glass apparatus was cleaned by immersion in dichromic-sulfuric mixture and washed with tap water prior to each run. Subsequently soaking and rinsing was made with distilled water and then with deionised water, followed by drying in an oven. The apparatus was assembled using silicone grease on the ground glass joints.

Shearing method employing a stopcock for the boundary formation was used in this work. Aqueous HCl and $ZnCl_2$ were used as leading and following solution respectively. Filling technique of the moving boundary cell was carried out as follow.

After the stopcock and anode unit were put in place, a long clean p.v.c. tubing of 0.1 mm i.d. was lowered down the moving boundary tube until it reached the bottom part of the anode compartment. The top end of this tube was connected to a 2 cm³ glass syringe. Repeated flushing of the anode compartment was made with the following solution of suitable concentration, followed by complete filling of the compartment up to about 1 cm above the lower stopcock. The lower stopcock was then turn 90° and the excess of the solution was removed. The rest of the cell was then rinsed with deionised water, followed by the leading solution. The cathode vessel was then connected and the whole cell was completely filled. After the silver-silver chloride electrode was put into place, the parts of the cell were held firmly together in a vertical position by a long glass support and rubber bands. The complete cell was lowered into the thermostat jacket and held vertical on the rubber base. A period of about half an hour was allowed for the cell to reach the bath temperature. Before the current was started, the lower stopcock was restored to the upright position and the junction between the bottom following and top leading solutions was formed.

For the run with moderate concentration and at the current exceeding 5 mA the boundary was easily located and the electrolysis was stopped after the boundary had passed the ball and cup joint. For dilute solutions at the current below 2 mA, when the

boundary was not visible, a further 10 - 20 minutes was allowed for the electrolysis. To ensure the passage of the boundary, the sample of the solution above the ball and cup joint was tested with 0.5 mol kg^{-1} NaOH. A white suspension of zinc hydroxide or hydroxychloride indicated the presence of zinc in the solution.

After electrolysis was complete, the circuit was disconnected and the cell was carefully lifted out of the bath. The upper tube was tilted about 30° from the original upright position, and the stopcock was turned to 90° to isolate the following solution in the middle section. This solution was allowed to equilibrate with room temperature before analysis took place.

3.6.2 Analysis

The concentrations of the adjusted indicator solutions were determined by external conductometric analysis. This method involved sampling and conductance measurements. These techniques are described as follow :

3.6.2.1 Sampling

The solution in the cell was equilibrate with the room temperature for at least half an hour before sampling was commenced.

After the cathode vessel had been disconnected, the solution above the ball and cup joint was discarded. The solution in the middle section down to a level 1-2 cm below the joint was removed. A long p.v.c. tubing at the end of 2 cm^3 syringe was inserted in to the middle section and the top half of the solution was withdrawn. This sample was deliver into the 10 cm^3 weight pipet, which was then weighed. The second half of the

solution was also removed in the same way leaving the solution 2 cm above the top stopcock. A second weight pipet was used for this sample. In most cases, about 3g of solution sample was delivered each time and was subsequently weight diluted to 50 g. Conductances of these solutions were determined in the same way as described in section 3.5.1.

When only a single sample was to be analysed, the solution 2 cm below the joint down to 2 cm above the stopcock was withdraw.

3.6.2.2 Conductance Measurements

After sampling, conductance measurements of the solutions were made. Standard techniques for conductance measurements described in section 3.5.1 were strictly followed. Deionised water stored overnight in a p.v.c. container was used for weight dilutions.

3.6.2.3 Calculation of the Kohlrausch Concentration

Calculations of conductances from resistance measurements were described in section 3.5.4 . The approximate concentration of an analysed solution was obtained by the interpolation of the conductance vs. concentration chart of $ZnCl_2$ solutions. The exact concentration of this solution was deduced by the successive approximation method using deviation function vs. concentration equation. The concentration of the following solution was then calculated from weight dilution. Detail of the method is in Appedix 1, 2, 3.

3.6.3 Calculation Of the Transference Number

The volume corrected transference number (12) of the following zinc ion-constituent is calculated from equation (3.3),

$$T_{Zn} = \frac{T_H m_{Zn} |Z_{Zn}|}{m_H |Z_H|} \quad (3.3)$$

T_H was obtained from the data of T_H^{HCl} vs. concentration for HCl solution in Miller's paper (45).

m_H was obtained from the solution preparation by weight dilution of stock solution.

m_{Zn} was the result from the analysis of the sample by conductance measurements.

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