# CHAPTER IV

# EXPERIMENTAL RESULTS

## 4.1 Electrode Calibration

### 4.1.1 The Hydrogen Electrode

The calibration of hydrogen electrode was carried out by measuring the emf. against the calomel electrode in the cell,

$$Pt,H_2(P) \ / \ HCl(C) \ // \ 0.1 \ M.KCl \ / \ HgCl_2, \ Hg \qquad (I)$$

The experimental emf.s data were listed in Table 4.1

**Table 4.1** The observed emf.s at range of temperature as a function of hydrochloric acid concentration.

| $C_{HCl}$ (mol $dm^{-3}$) | $E_{cell}$ (V.) | Temp.( °C.) |
|---|---|---|
| 0.01124 | 0.4499 | 25.90 |
| 0.02066 | 0.4344 | 25.88 |
| 0.03069 | 0.4249 | 25.92 |
| 0.04056 | 0.4180 | 25.72 |
| 0.05044 | 0.4130 | 25.84 |
| 0.06077 | 0.4181 | 25.70 |

The electrode potential of the calomel electrode ($E_{cal}$) was calculated by using the equation

$$E_{cell} = E_{cal} - E_H$$

$$= E_{cal} - E_H^{\circ} + (RT/F)\ln m_{HCl}\gamma_{\pm}$$

$$E_{obsd} = E_{cal} - E_H^{\circ} + (RT/F)\ln m_{HCl}\gamma_{\pm}$$

$$E_H^{\circ} = 0 \ ;$$

therefore $$E_{cal} = E_{obsd} - (RT/F)\ln m_{HCl}\gamma_{\pm}$$

The experimental data and the result of the calculation were listed in Table 4.2. Included in the Table are the differences between the reference and the measured values. These difference result from the partial surface pressure of electrolyte solution and the effect of solution becoming supersaturated with dissolve hydrogen gas. However, it was difficult to determine the value of these effects. Muju (16) suggested that, for certain concentration range, the correction value of these effects was constant. He introduced the indirect method to determine this value by comparing the experimental value of cell I, at various concentrations with the reference value (at the same temperature). In this work, the difference of the potential values was fairly constant. The mean value of 0.0030 volt. was taken as the correction to the measured potential of the cell

$$Pt,H_2\ (P)\ /\ HX(C)\ /\ AgX,Ag \qquad (II)$$

in the subsequent experiment.

4.1.2 The Silver-silver Halide Electrodes

The observed emfs. of cell II at 25°C are shown in Tables 4.3 and 4.4. Each of the measured potentials of cell E was corrected by adding the value of 0.0030 volt. The standard potential of the silver-silver halide electrodes, $E^{\circ}$, were determined from the equation

$$E' = E^{\circ} - A\,C^{1/2} \qquad (16)$$

where $E' = E_{corr} + (2RT/F)\ln C$ which can be calculated from the experimental data and A is the constant value in term of mean ion activity coefficient $\gamma_{\pm}$ (17). The former term, when plotted against $C^{1/2}$, gives a straight line of slope A and the intercept $E^{\circ}$, the standard potential of the silver-silver halides electrode. The calculated $E'$ value for systems of silver-silver chloride and bromide were listed in the Tables 4.5 and 4.6 respectively. The extrapolation of the linear plot of $E'$ versus $C^{1/2}$ for these systems were shown in Figs.4.1 and 4.2 .

## 4.2 Electromotive Force Data

The electromotive force of the cells

$$Zn\text{-}Hg \;/\; ZnX_2\ (m_1) \;/\; AgX,Ag \qquad (III)$$

and

$$Zn\text{-}Hg \;/\; ZnX_2\ (m_1),\ KX(m_2) \;/\; AgX,Ag \qquad (IV)$$

were listed in Tables 4.7,4.8,4.9, and 4.10

The relationship between the emf and the concentration of $ZnX_2$ of cell III were shown in Figs 4.3 and 4.4

Table 4.2 The calculated electrode potential of the calomel electrode

| $C_{HCl}$ mol $dm^{-3}$ | $\gamma\pm$ ref(15) | Eobsd. V. | $E_{cal}$ V. | $E_{ref}-E_{cal}$ V. |
|---|---|---|---|---|
| 0.01124 | 0.901 | 0.4494 | 0.3308 | 0.0029 |
| 0.02066 | 0.869 | 0.4343 | 0.3308 | 0.0030 |
| 0.03089 | 0.843 | 0.4249 | 0.3307 | 0.0030 |
| 0.04056 | 0.834 | 0.4179 | 0.3307 | 0.0030 |
| 0.05044 | 0.826 | 0.4125 | 0.3307 | 0.0030 |
| 0.06077 | 0.819 | 0.4080 | 0.3308 | 0.0029 |

$E_{ref}$ = 0.3337 V. (12)

$E_{mean}$ = 0.0030 V.

Table 4.3 The observed emf.s of the cell, $Pt,H_2(P)/HCl(C)/AgCl,Ag$ at 25 ° C.

| $C_{HCl}$ (mol $dm^{-3}$) | emf (V.) |
|---|---|
| 0.00599 | 0.4849 |
| 0.00792 | 0.4735 |
| 0.01075 | 0.4557 |
| 0.01597 | 0.4361 |
| 0.02027 | 0.4245 |
| 0.02657 | 0.4111 |
| 0.03164 | 0.4026 |
| 0.04101 | 0.3899 |
| 0.05099 | 0.3797 |

Table 4.4 The observed emf.s of the cell, $Pt,H_2(P)/HBr(C)/AgBr,Ag$ at 25° C.

| $C_{HBr}$ (mol $dm^{-3}$) | emf (V.) |
|---|---|
| 0.00526 | 0.3394 |
| 0.01040 | 0.3060 |
| 0.01542 | 0.2865 |
| 0.01906 | 0.2759 |
| 0.02854 | 0.2563 |
| 0.03385 | 0.2480 |
| 0.03912 | 0.2412 |
| 0.04833 | 0.2310 |

Table 4.5 Experimental data and calculated $E'$ values of silver-silver chloride electrode.

| $c^{1/2}$ $mol^{1/2}\ dm^{-3/2}$ | $E_{corr}$ V. | $E'$ V. |
|---|---|---|
| 0.07739 | 0.4879 | 0.2249 |
| 0.08675 | 0.4765 | 0.2254 |
| 0.10368 | 0.4587 | 0.2258 |
| 0.12637 | 0.4391 | 0.2265 |
| 0.14238 | 0.4275 | 0.2272 |
| 0.16319 | 0.4141 | 0.2277 |
| 0.17789 | 0.4056 | 0.2281 |
| 0.20251 | 0.3929 | 0.2288 |
| 0.22581 | 0.3827 | 0.2298 |

$$E^{\circ}_{meas} = 0.2222 \text{ V.}$$
$$E^{\circ}_{ref} = 0.22239 \text{ V.} \quad (18)$$

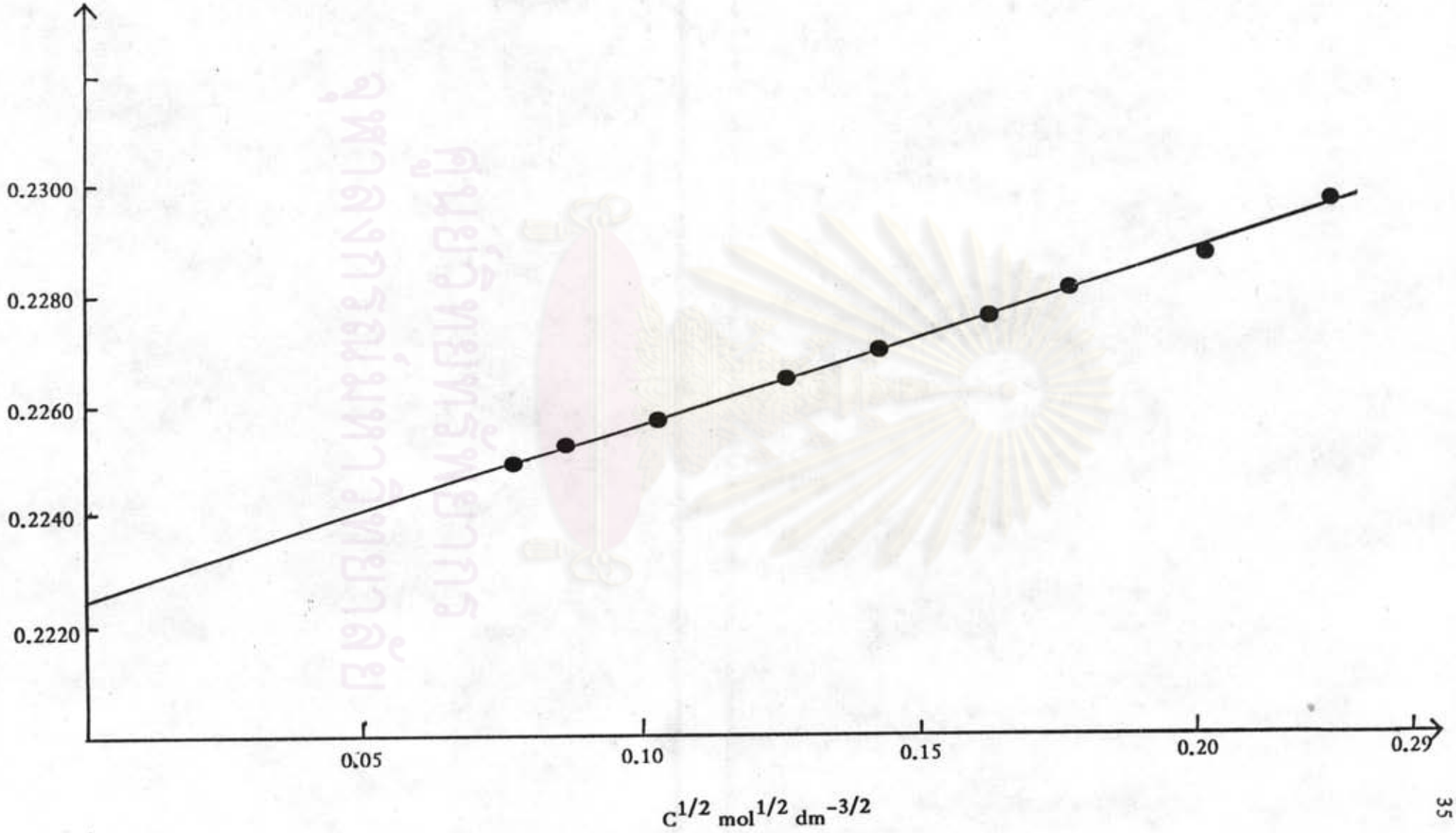


Figure 4.1 The extrapolation of the linear plot of $E'$ vs $C^{1/2}$ of the cell $H_2$ (P) / HCl (C) / AgCl, Ag

Table 4.6 Experimental data and calculated $E'$ values of silver-silver bromide electrode

| $c^{1/2}$ $mol^{1/2}\ dm^{-3/2}$ | $E_{corr}$ V. | $E'$ V. |
|---|---|---|
| 0.07257 | 0.3424 | 0.0732 |
| 0.10202 | 0.3090 | 0.0748 |
| 0.12419 | 0.2895 | 0.0755 |
| 0.13806 | 0.2789 | 0.0758 |
| 0.16894 | 0.2593 | 0.0770 |
| 0.18400 | 0.2510 | 0.0774 |
| 0.19788 | 0.2442 | 0.0780 |
| 0.21994 | 0.2340 | 0.0788 |

$E^{\circ}_{meas}$ = 0.0708 V.

$E^{\circ}_{ref}$ = 0.07112 V. (18)

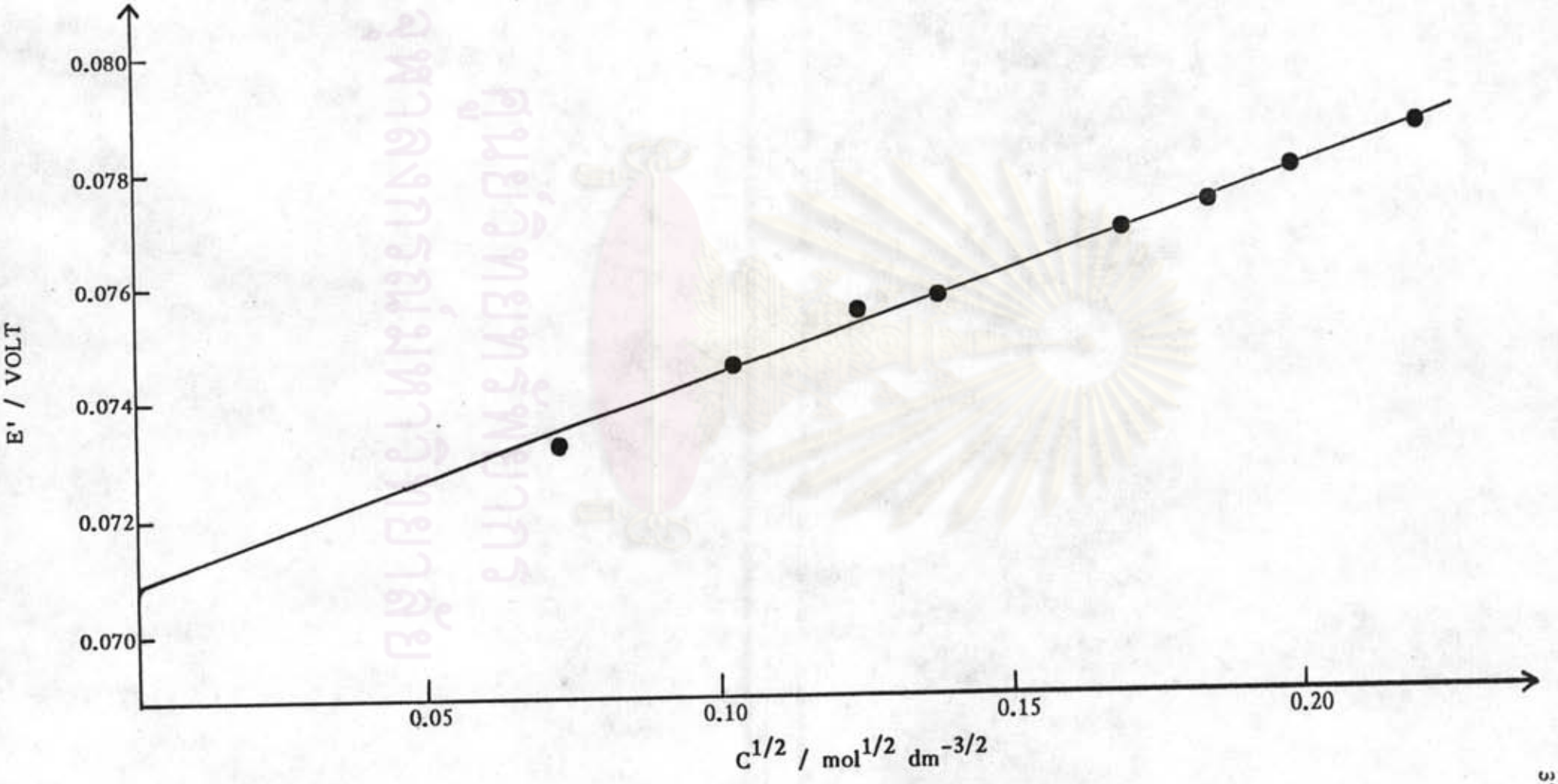


Figure 4.2 The extrapolation of the linear plot of $E'$ vs $C^{1/2}$ of the cell Pt, $H_2$ (P) / HBr (C) / AgBr, Ag

Table 4.7 The electromotive force measurements of cell(III) for various $ZnCl_2$ concentrations.

| m mol $kg^{-1}$ | $E_{measd.}$ V. | m mol $kg^{-1}$ | $E_{measd.}$ V. |
|---|---|---|---|
| 0.00098 | 1.2378 | 0.37307 | 1.0386 |
| 0.00294 | 1.1988 | 0.49003 | 1.0300 |
| 0.00366 | 1.1910 | 0.54438 | 1.0270 |
| 0.00442 | 1.1841 | 0.60653 | 1.0233 |
| 0.00508 | 1.1793 | 0.68557 | 1.0200 |
| 0.00735 | 1.1672 | 0.78735 | 1.0158 |
| 0.00827 | 1.1632 | 0.84448 | 1.0137 |
| 0.01039 | 1.1555 | 0.89037 | 1.0124 |
| 0.01204 | 1.1504 | 0.93123 | 1.0113 |
| 0.01549 | 1.1423 | 0.97995 | 1.0096 |
| 0.02052 | 1.1331 | 1.09970 | 1.0065 |
| 0.02201 | 1.1308 | 1.29992 | 1.0017 |
| 0.03017 | 1.1206 | 1.40031 | 0.9994 |
| 0.04243 | 1.1096 | 1.50247 | 0.9970 |
| 0.05913 | 1.0993 | 1.60265 | 0.9953 |
| 0.06549 | 1.0960 | 1.70085 | 0.9935 |
| 0.08327 | 1.0883 | 1.89969 | 0.9899 |
| 0.09203 | 1.0850 | 1.98896 | 0.9886 |
| 0.10352 | 1.0812 | 2.07495 | 0.9870 |
| 0.15817 | 1.0673 | 2.34061 | 0.9830 |
| 0.19300 | 1.0604 | 2.61177 | 0.9789 |
| 0.20987 | 1.0545 | 2.94767 | 0.9743 |
| 0.32792 | 1.0433 | 3.22138 | 0.9710 |

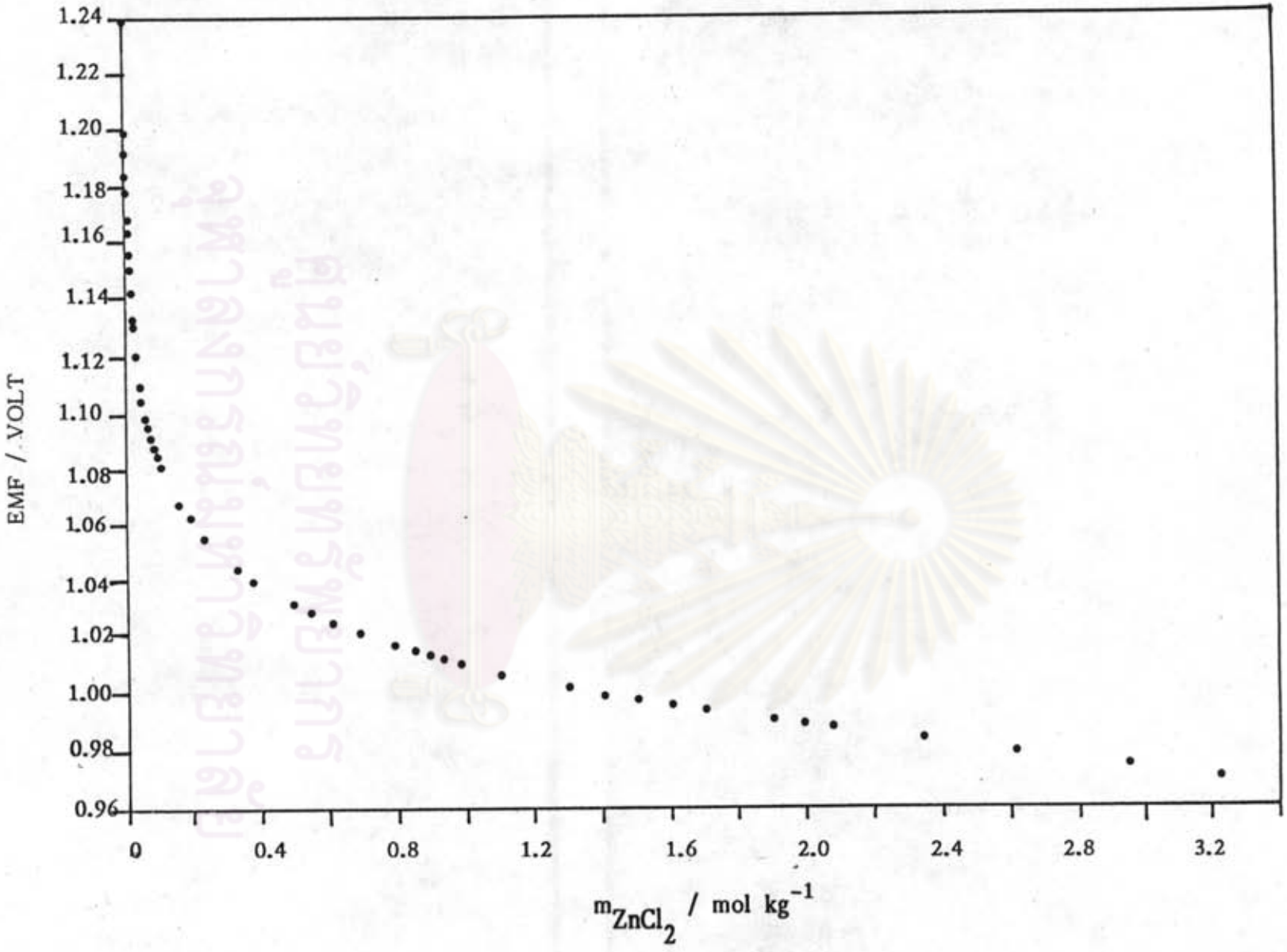


Figure 4.3 The plot of relationship between the emf and the concentration of $ZnCl_2$ of cell III

Table 4.8 The electromotive force measurements of cell IV for the solution mixture ($ZnCl_2$ - KCl) at various Zn : Cl ratios.

| total zinc mol $kg^{-1}$ | total chloride mol $kg^{-1}$ | emf V. |
|---|---|---|
| 0.02889 | 0.57676 | 1.0747 |
| 0.03261 | 0.58623 | 1.0730 |
| 0.03339 | 0.56697 | 1.0727 |
| 0.03730 | 0.59692 | 1.0709 |
| 0.04353 | 0.61069 | 1.0686 |
| 0.05232 | 0.62693 | 1.0655 |
| 0.06551 | 0.65628 | 1.0619 |
| 0.07521 | 0.68174 | 1.0596 |
| 0.08762 | 0.70125 | 1.0572 |
| 0.10538 | 0.73905 | 1.0539 |
| 0.13224 | 0.79484 | 1.0499 |
| 0.17737 | 0.88717 | 1.0443 |
| 0.25838 | 1.03489 | 1.0371 |
| 0.29268 | 0.87823 | 1.0386 |
| 0.58117 | 2.11513 | 1.0153 |
| 0.74772 | 1.99442 | 1.0130 |
| 0.90005 | 2.29549 | 1.0088 |

Table 4.9 The electromotive force measurements of cell (III) for various $ZnBr_2$ concentrations.

| m mol $kg^{-1}$ | $E_{measd.}$ V. | m mol $kg^{-1}$ | $E_{measd.}$ V. |
|---|---|---|---|
| 0.00100 | 1.0854 | 0.56246 | 0.8631 |
| 0.00203 | 1.0596 | 0.58149 | 0.8617 |
| 0.00400 | 1.0361 | 0.64224 | 0.8579 |
| 0.00510 | 1.0274 | 0.67096 | 0.8563 |
| 0.00762 | 1.0135 | 0.70318 | 0.8541 |
| 0.00822 | 1.0110 | 0.80044 | 0.8492 |
| 0.01281 | 0.9960 | 0.92025 | 0.8432 |
| 0.01887 | 0.9832 | 0.99049 | 0.8401 |
| 0.02500 | 0.9740 | 1.01024 | 0.8397 |
| 0.03210 | 0.9660 | 1.30092 | 0.8295 |
| 0.04000 | 0.9590 | 1.49993 | 0.8235 |
| 0.05000 | 0.9515 | 1.65193 | 0.8192 |
| 0.05705 | 0.9470 | 1.82372 | 0.8158 |
| 0.07289 | 0.9390 | 1.97743 | 0.8124 |
| 0.09000 | 0.9320 | 2.13239 | 0.8093 |
| 0.10000 | 0.9278 | 2.24645 | 0.8072 |
| 0.15000 | 0.9145 | 2.48530 | 0.8028 |
| 0.20269 | 0.9033 | 2.69102 | 0.7991 |
| 0.28113 | 0.8910 | 2.71177 | 0.7989 |
| 0.33976 | 0.8844 | 2.89758 | 0.7962 |
| 0.38082 | 0.8797 | 3.09691 | 0.7929 |
| 0.45553 | 0.8724 | 3.30599 | 0.7901 |
| 0.48207 | 0.8697 | 3.55661 | 0.7861 |

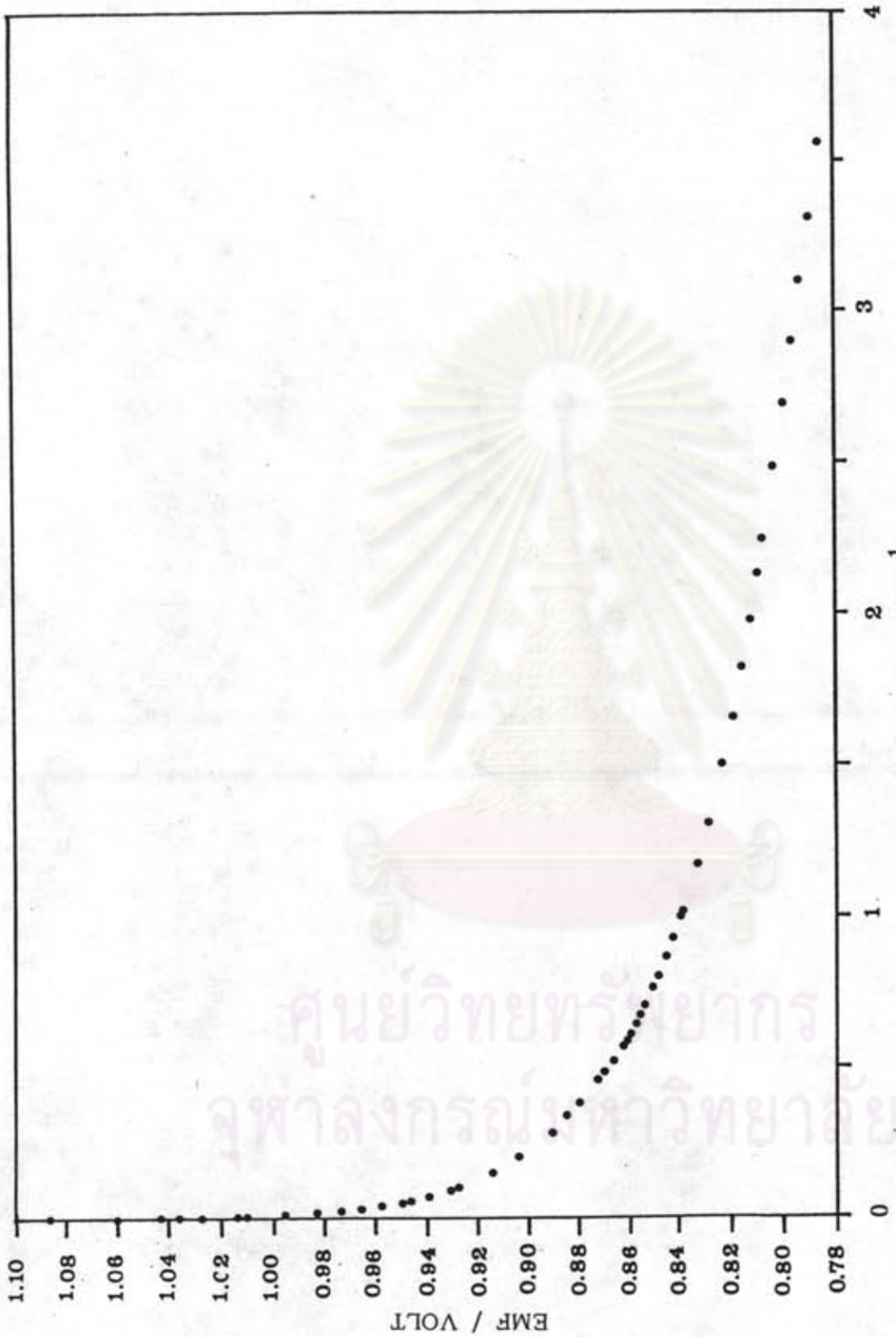


Figure 4.4 The plot of relationship between the emf and the concentration of $ZnBr_2$ of cell III

Table 4.10 The electromotive force measurements of cell IV for the solution mixtures ($ZnBr_2$ + KBr) at various Zn : Br ratios.

| total zinc mol $kg^{-1}$ | total bromide mol $kg^{-1}$ | emf. V. |
|---|---|---|
| 0.02339 | 0.57921 | 0.9232 |
| 0.02941 | 0.55729 | 0.9210 |
| 0.03301 | 0.56695 | 0.9182 |
| 0.04098 | 0.58164 | 0.9144 |
| 0.06249 | 0.62481 | 0.9083 |
| 0.07026 | 0.64086 | 0.9057 |
| 0.09970 | 0.69967 | 0.9005 |
| 0.14946 | 0.79890 | 0.8918 |
| 0.20753 | 0.91517 | 0.8816 |
| 0.29614 | 1.10789 | 0.8737 |
| 0.44097 | 1.38203 | 0.8632 |
| 0.55054 | 1.80120 | 0.8520 |
| 0.60742 | 1.87387 | 0.8493 |
| 0.72267 | 1.94524 | 0.8451 |
| 0.85016 | 2.40079 | 0.8382 |