Potentiometric Measurement of Standard Potential of Mercury and Ion-pair Formation Constants of Mercuric Halides in Anhydrous Ethylenediamine.

by

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에틸렌디아민 非水溶液中에서의 水銀電極의 標準電位 및 水銀鹽化鹽의 Ion-Pair 恒數測定

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金 俊 容

요 약

非水溶液 Ethylenediamine 中에서 水銀電極의 標準電位 및 水銀鹽化物, HgCl₂, HgBr₂, HgI₂의 Ion-Piar 形成 恒數를, Hg 電極/HgX₂ 또는 HgX₂+NaX//亞鉛아마르감 參照電極과 같은 Cell 의 構成으로서 電位差法에 依하여 測定하였다.

INTRODUCTION

As previously reported by Schaap and co-workers,[1] it has been shown that, at ordinary concentrations, ion-pair formation is important in anhydrous ethylenediamine and that a knowledge of association constant is a prerequiste to any quantitative treatment of ionic equilibria, potentiometric behavior, and polaro-graphic half-wave potentials in the solvent.
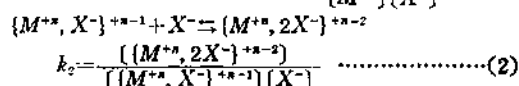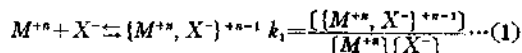
Conductometric[2] and potentiometric measurements [3] on a large number of uni-univalent electrolytes have been reported. As an example of di-univalent electrolytes, Peacock, Schmidt and Schaap[4] reported concuctance and viscosity studies of mercnric bromide, iodide and cyanide solutions in ethylenediamine.

It is the purpose of this paper to derive equations applicable to solvents of low dielectric constant. In order to make accurate calculations of the effect of electrolyte concentration on cell potentials, it is necessary to know the association constants of salts, activity coefficients, liquid junction potentials, and the reference electrode in ethylenediamine.
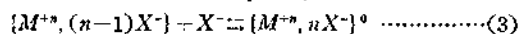
THEORETICAL

Equilibria in MX$_n$ Solution. The step-wise ion-pair association equilibria involving the cation, M^{+n}, and anion, X^-, may be represented as follows:

$$M^{+n}+X^- \leftrightarrows \{M^{+n}, X^-\}^{+n-1} \quad k_1=\frac{[\{M^{+n}, X^-\}^{+n-1}]}{[M^{+n}][X^-]}\cdots(1)$$

$$\{M^{+n}, X^-\}^{+n-1}+X^- \leftrightarrows \{M^{+n}, 2X^-\}^{+n-2}$$

$$k_2=\frac{[\{M^{+n}, 2X^-\}^{+n-2}]}{[\{M^{+n}, X^-\}^{+n-1}][X^-]} \quad\cdots\cdots\cdots\cdots(2)$$

Finally, the last association step results in the

formation of the neutral species, i.e.,

$$\{M^{+n}, (n-1)X^-\} + X^- \rightleftharpoons \{M^{+n}, nX^-\}^0 \quad \cdots\cdots(3)$$

$$k_n = \frac{\{\{M^{+n}, nX^-\}\}}{\{\{M^{+n}, (n-1)X^-\}\}\{X^-\}}$$

$$= \frac{\{\{M^{+n}, nX^-\}\}}{k_1 k_2 \cdots k_{n-1}[M^{+n}][X^-]^n} \quad \cdots\cdots(4)$$

where ion pairs are enclosed in braces, and square brackets denote activities. Further association of the neutral species to form triple ions, quardruples ions, and higher polymeric species will not be considered in this derivation.

If the total stoichiometric concentration of metal ion present in all forms is $\sum_M$, then in terms of the concentration of each individual species,

$$\sum_M = \frac{[M^{+n}]}{f_M} + \frac{\{\{M^{+n}, X^-\}\}}{f_{MX}} + \frac{\{\{M^{+n}, 2X^-\}\}}{f_{MX_2}} +$$
$$\cdots \frac{\{\{M^{+n}, nX^-\}\}}{f_{MX_n}} \quad \cdots\cdots(5)$$

then,

$$\sum_M = [M^{+n}]\left\{ \frac{1}{f_M} + \frac{k_1[X^-]}{f_{MX}} + \frac{k_1 k_2[X^-]}{f_{MX_2}} + \cdots \right.$$
$$\left. + \frac{k_1 k_2 \cdots k_{n-1}[X^-]}{f_{MX_n}} \right\} \quad \cdots\cdots(6)$$

This equation may be expressed more conveniently by the general relationship,

$$\sum_M = [M^{+n}] \sum_{j=0}^{n} \frac{K_j[X^-]^j}{f_{MX_j}} \quad \cdots\cdots(7)$$

where $K_j = k_1 k_2 k_3 \cdots k_{n-1} k_n$, $K_1 = 1$ by definition, and f_M, f_{MX}, $f_{MX_2} \cdots$ and f_{MX_n} are the activity coefficients of the successively formed species.

Substituting the expression for $[M^{+n}]$ into the Nernst equation for a metal-metal ion electrode,

$$E_M = E^0 + E_j + \frac{RT}{nF} \ln \frac{\sum_M}{\sum_{j=0}^{n} \frac{K_j[X^-]^j}{f_{MX_j}}} \quad \cdots\cdots(8)$$

At low concentrations, where a less associated species exist in appreciable amounts, a plot of E_M versus $\log \sum_M$ should be curved, with the slope approaching 0.05916/n at the lower of concentration(25°C).

In the limit of higher concentrations, where association to the uncharged species $\{M^{+n}, nX^-\}$ may be assumed to almost complete, and $\sum_{X^-} = n\sum_M + n$, the activity of the metal ion is given by

$$[M^{+n}] = \left(\frac{\sum_M}{n^n K_n} \right)^{1/(n+1)} \quad \cdots\cdots(9)$$

and the Nernst equation becomes,

$$E_M = E^0 + E_j - \frac{RT}{n(n+1)F} \ln(n^n K_n) + \frac{RT}{n(n+1)F}$$

$$\ln \sum_M \quad \cdots\cdots(10)$$

At sufficiently high concentrations the limiting slope of a plot of E_M versus $\log \sum_M$ will be 0.05916/n(n+1) at 25°C.

Equilibria in Solutions of MX_n and SX. If a second, inert "supporting electrolyte" salt, SX, is present in solution and supplies essentially all of the anions, X^-, either through a greater degree of ionization or because of a much higher stoichiometric concentration, and if the ion-pair association constant of SX is known, then $[X^-]$ may be calculated by means of the following equation:[1]

$$[S^+] = [X^-] = \frac{(1 + 4\sum_{SX} K_{SX} f_i^2)^{1/2} - 1}{2K_{SX} f_i} \quad \cdots\cdots(11)$$

The Nernst equation for a metal-metal ion electrode, assuming that $[X^-]$ is governed solely by the excess inert salt, SX, may be represented

$$E_M = E^0 + E_j + \frac{RT}{nF} \ln \sum_M - \frac{RT}{nF} \ln \sum_{j=0}^{n} K_j$$

$$\left\{ \frac{(1 + 4\sum_{SX} K_{SX} f_i^2)^{\frac{1}{2}} - 1}{2K_{SX} f_i} \right\}^j / f_{MX_j} \quad \cdots\cdots(12)$$

If the neutral species, MX_n, predominates, then

$$E_M = E^0 + E_j + \frac{RT}{nF} \ln \frac{\sum_M}{K_n}$$

$$- \frac{RT}{F} \ln \frac{(1 + 4\sum_{SX} K_{SX} f_i^2)^{1/2} - 1}{2K_{SX} f_i} \quad \cdots\cdots(13)$$

If dissociation of MX_n and SX are both neglected, i.e., if $4\sum_{SX} K_{SX} f_i^2 \gg 1$, equation 13 simplifies to

$$E_M = E^0 + E_j + \frac{RT}{nF} \ln \frac{\sum_M}{K_n} + \frac{RT}{2F} \ln \frac{K_{SX}}{SX} \quad \cdots(14)$$

Equation 14 gives the dependence under these conditions of E_M upon $\sum_M$, $\sum_{SX}$, and the ion-pair formation constants. The last term is independent of n. The relation between E_M and $\sum_{SX}$ is seen to be independent of the charge on the electroactive species, M^{+n}.

Subtracting equations 10 and 14, the difference of potential between measurements made at different values of $\sum_M$ is given by:

$$\Delta E = \frac{RT}{(n+1)F} \ln K_n - \frac{RT}{n(n+1)F} \ln n^n$$

$$- \frac{RT}{2F} \ln \frac{K_{SX}}{\sum_{SX}} + \frac{RT}{nF} \ln \frac{(\sum_M)^{1/n}}{\sum_M} \quad \cdots(15)$$

If $\sum_M$ is the same for both points:

$$\Delta E = \frac{RT}{(n+1)F} \ln \frac{K_n}{n\sum_M} - \frac{RT}{2F} \ln \frac{\sum_{SX}}{K_{SX}} \quad \cdots(16)$$

At higher concentration of MX_n, i.e., above $10^{-2}M$,

K_n may be evaluated from $\triangle E$ if K_{SX} is known.

EXPERIMENTAL

Chemicals. -All chemicals were of reagent grade and were not purified further except the Eastman Kodak ethylenediamine, which was distilled twice under nitrogen from sodium at reduced pressure.

Potentiometric Methods. -Reference Electrode[6]. A calomel electrode could not be prepared in ethylenediamine because mercurous chloride instantaneously react with ethylenediamine to give a black precipitate. The zinc amalgam zinc chloride reference electrodes were prepared by contacting two-phase zinc amalgam with ethylenediamine saturated with zinc chloride, saturated with either LiCl or NaCl. electrode may be represented,

Ethylenediamine saturated | ZnCl | Zn-Hg
with LiCl or NaCl | (solid) | (two-phase)
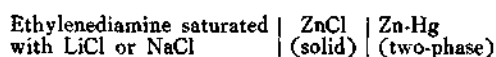
At 25°C, the half-cell potential is

$E = E^O_{Hg-Zn} + 0.0296 \log K_{sp} - 0.059 \log a_{Cl}^-$

where $E^*_{Hg-Zn} + 0.0296 \log K_{sp}$ is equal to the standard potential of the saturated $ZnCl_2$ zinc amalgam electrode. Theoreticaly, the difference in potential between zinc amalgam zinc chloride containing LiCl

Fig. 1. Three-compartment cell for electrochemical measurements in ethylenediamine; e₁, mercury indicator electrode; e₂, zinc amalgam zinc chloride reference electrode.

and NaCl at the same concentrations is calculated to be 3 millivolts.

Half-Cell. Three-compartment cell for electrochemical measurements in anhydrous ethylenediamine was used as shown in Figure 1.

E. m. f. Determination. The mercury electrode half-cell was filled and assembled in dry box under nitrogen atmosphere. The solutions were saturated immediately with nitrogen and half-cell was placed in thermostat at 25°C until temperature equilibrium was attained. Then, a current of nitrogen was allowed to stream through the solution for about 5 min. before taking the e. m. f. reading. E. m. f. values then were recorded every 5 to 10 min. by potentiometer.

RESULTS AND DISCUSSION

The step-wise ion-pair formation constants of the associated species. $HgBr^+$, $HgBr_2$, $HgCl^+$, $HgCl_2$ and HgI_2 were determined from potential data obtained with a mercury indicator electrode. Electromotive force measurements of the cell

Hg pool, | HgX₂ or HgX₂÷NaX | Saturated NaCl, sat. ZnCl₂, 2-phase zinc amalgam reference electrode
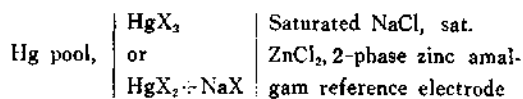
have been made in ethylenediamine.

The data were obtained for three separate series of experiments. In the first series, mercuric halides were titrated from a buret into 50 ml. of anhydrous ethylenediamine. In the second series, where a supporting electroyte was present, the titrant contained mercuric halides and the same concentration of supporting electrolyte, retaining a constant concentration of supporting electrolyte. In the third series, the initial solution contained mercury halide, and the titrant contained a supporting electrolyte salt, NaX, which provided a much higher stoichiometric electrolyte concentration of X⁻, the common anion.

In order to determine the standard potential of the mercury indicator electrode, the association constant of HgCl₂ HgBr₂ and HgI₂ were evaluated from equation 15. With these values of the association constants, the standard potential of the mercury indicator electrode was calculated from equations 10. 13 and 14. The average value of the standard potential for HgBr₂, HgCl₂ and HgI₂ is calculated to be 1.4552
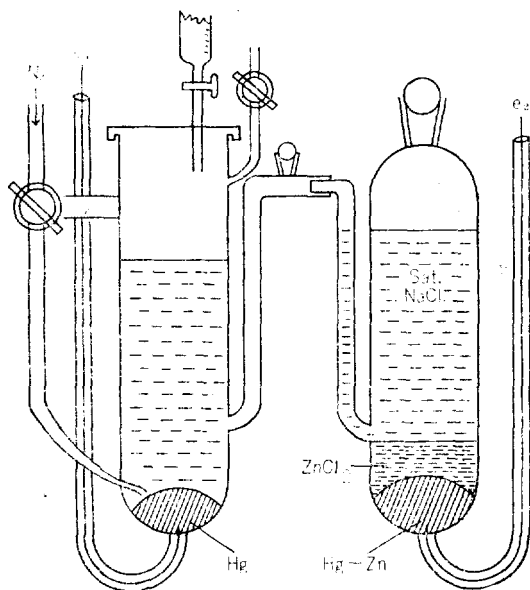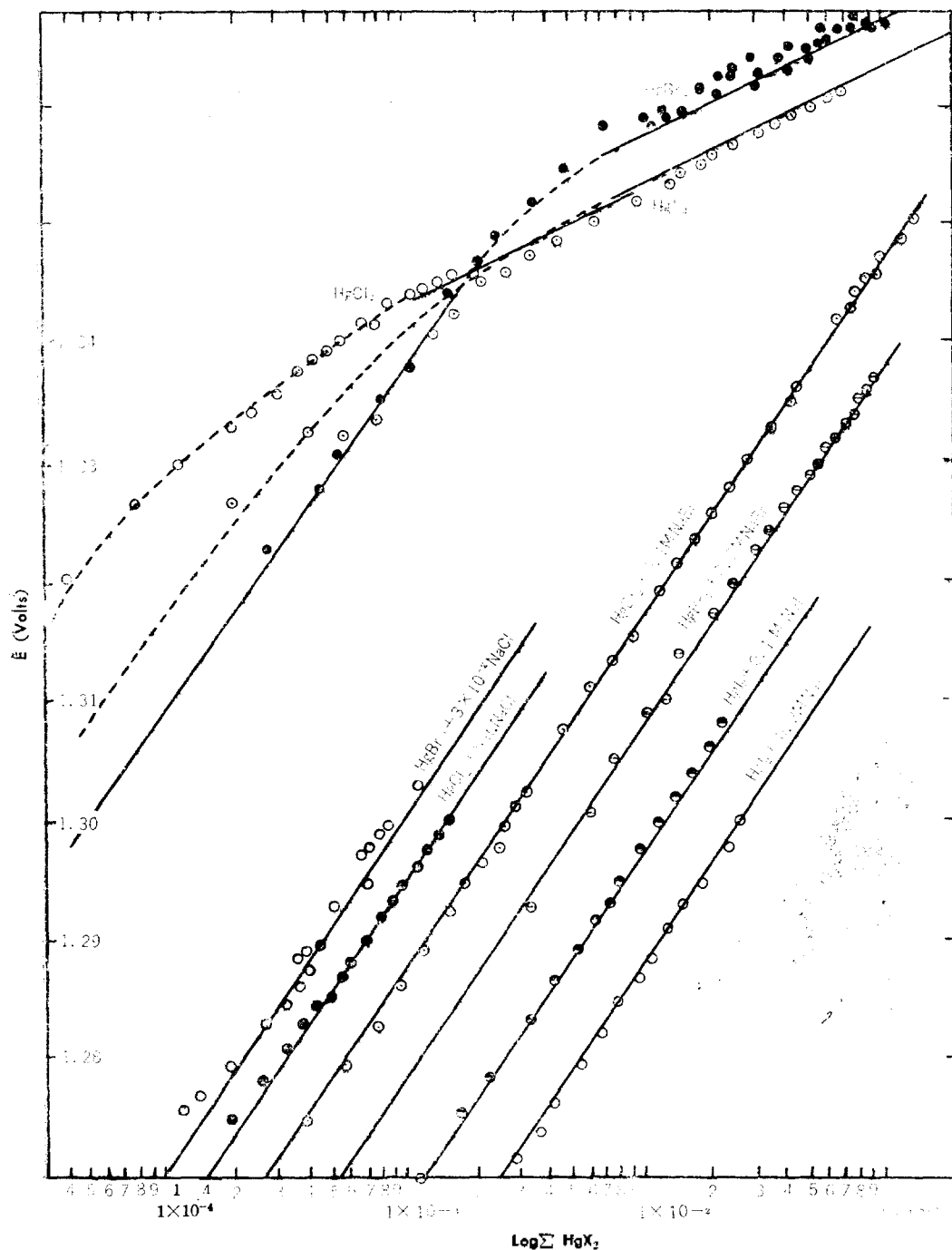
Fig. 2. Relations of E volts with log $\sum_{HgX_2}$.
Points are experimental and solid lines are theoretical.

volts vesrus the saturated NaCl-zinc chloride zinc amalgam reference electrode.

Using $E^0 = 1.4552$ volts, the over-all ion-pair for-

mation constants of the mercuric halides, $HgCl_2$, $HgBr_2$ and HgI_2 were evaluated to be 4.76×10^7, 1.72×10^7, and 4.24×10^7, respectively.

Typical curves calculated for the titrations of $HgCl_2$, $HgBr_2$ and HgI_2, both in the presence and absence of higher concentrations of excess common anion salts such as NaBr, NaCl, and NaI are shown in Figure 2. In each case the points are experimental and the solid lines are theoretical. As expected from the theoretical considerations, the slopes of E_M versus $\log \sum_{HgX_2}$ plots, in the absence and presence of a high concentration of supporting electrolyte, are 10 and 29.6 millivolts, respectively.

TABLE 1. Over-All Ion-Pair Formation Constants of Mercuric Halides($E^0=1.4552$ volts, at $25°C$)

Electrolytes	E^0	K_{HgX_2}	Ion-Pair Formation Constants used
$HgCl_2$	1.4572	4.76 x 10^7	NaCl=8400
$HgBr_2$	1.4553	1.72 x 10^7	NaBr=3740
HgI_2	1.4531	4.24 x 10^7	NaI=1940

On the other hand, the mathematical treatment for the determination of ion-pair formation constants of polyvalent cations is similar to the DeFord and Hume[6] approach to the evaluation of consecutive formation constants of complex ions. The consecutive formation constants are expresed by the following equation,

$$k_1 = [HgX^+]/[Hg^{++}][X^-]$$
$$k_2 = HgX_2/[HgX^+][X^-]$$

If the symbol $F_0(X)$ is introduced for convenience to represent, then the metal-metal ion electrode potential may be represented as follows,

$$F_0(X) = \frac{1}{f_M} + \frac{k_1[X^-]}{f_{MX_1}} + \frac{k_1k_2[X^-]}{f_{MX_2}}$$
$$+ \cdots \frac{k_1k_2\cdots k_n[X^-]^n}{f_{MX_n}}$$
$$= \text{antilog} \frac{E^0 + E_j + (0.059/n)\log\sum_M - E_M}{0.059/n} \quad \cdots\cdots(17)$$

where $E^0 + E_j$ represents the standard potential of the indicator electrode versus the refer ence electrode used and includes any liquid junction potential. At a constant low concentration of MX_n, if a potentiometric titration is carried out with supporting electrolyte, SX, as titrant. $F_0(X)$ may be calculated by means of equation assuming the following condition: (1) MX_n is more associated than SX, $(K_{MX_n} \gg K_{SX})^*$; (2) activity coefficients f_{MX}, f_{MX_2}, and f_{MX_n-1} are

assumed to be equal; (3) further association of the neutral species with anions to be form triple and quardruple ions are ignord. **

The F_0 (X) values thus calculated from equation 17 were plotted against the concentration of supporting electrolyte. By extrapolating the F_0 (X) plots to the zero concentration of supporting electrolyte, SX, $1/f_M$ is intercept at$(X^-) = 0$, and k_1 is the slope. If $k_1[X^-]/f_{MX}$ is divided by $[X^-]$ after transposing the term which contains $1/f_M$, a function $F_1(X)$ is defined as follows,

$$F_1(X) = \frac{F_0(X) - 1/f_M}{[X^-]}$$
$$= \frac{k_1}{f_{MX}} + \frac{k_1k_2[X^-]}{f_{MX_2}} + \cdots$$
$$+ \frac{k_1k_2\cdots k_n[X^-]^{n-1}}{f_{MX_n-1}} \quad \cdots\cdots\cdots(18)$$

As before, if $F_1(X)$ is plotted versus$[X^-]$ and extrapolated to $[X^-] = 0$, the value of $F_2(X)$ at the intercept is equal to the term, k_1/f_{MX}, where is the first association constant. The limiting slope of the $F_1(X)$ plot is k_2. This process is repeated until all the constants have been determined. The data obtained are listed in Table 2. For this calculation, K_{NaX} values of 3740 and 8400 were used for NaBr and NaCl, respectively. The value of standard potential of mercury indicator electrode used is 1.4552 volts versus saturated NaCl-zinc amalgam-zinc chloride reference electrode.

TABLE 2. Ion-pair formation constants of mercuric halides, $HgBr_2$ and by $HgCl_2$ by application of the DeFord and Hume method.

Electrolytes[a]	k_1	k_2	k_n
$HgCl_2$	1.13×10^3	3.19×10^4	3.61×10^7
$HgCl_2$	1.17×10^3	3.89×10^4	4.55×10^7
$HgBr_2$	1.60×10^3	8.90×10^3	1.69×10^7

a) At a given concentration of mercuric halides, the solutions were titrated with NaCl or NaBr.

*The values used are: $K_{HgBr_2} = 1.76 \times 10^7$, $K_{NaBr} = 3740$, and $K_{HgCl_2} = 4.76 \times 10^7$, $K_{NaCl} = 8400$.

**In the presence of added halide ions, species of the type $[MX_{n+1}]^{-1}$, $[MX_{n+2}]^{-2}$, $\cdots[MX_{n+n}]^{-n}$ became very important. The stability of these species increases regularly with increasing concentration of cation or anion, maximum stability being achived the $[MX_{n+n}]^{-n}$ ion.

As shown in Table 2, the over-all ion-pair formation constants of mercuric halides are well agree with that of the Table 1.

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